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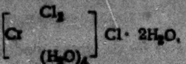
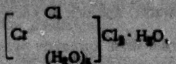
THE HYDRATES OF CHROMIUM CHLORIDE

A. V. Pamfilov and N. N. Gumenyuk

Two hydrates of chromium chloride are well known. In recent textbooks [1,2] mention is made of three hexahydrates differing in properties and in particular in their ability to react in aqueous solution with different amounts of silver ions. The respective structural formulas assigned to them are:



$$\left[\mathrm{Cr}\begin{matrix}\mathrm{Cl_2}\\ \\ \mathrm{(H_2O)_4}\end{matrix}\right]\mathrm{Cl}\cdot 2\mathrm{H_2O},$$



$$\left[\mathrm{Cr}\begin{matrix}\mathrm{Cl}\\ \\ \mathrm{(H_2O)_5}\end{matrix}\right]\mathrm{Cl_2}\cdot\mathrm{H_2O},$$

$[\mathrm{Cr(H_2O)_6}]\mathrm{Cl_3}$.

(I) Green modification of Werner and Recoura

(II) Green modification of Bjerrum

(III) Grey modification

This mode of presentation is evidently borrowed from Werner's monograph [3]. Wyrouboff [4] claims the existence of a still larger number of isomers. Reports in the literature are conflicting. Werner and Gubser [5] suggest that the amount of precipitated chlorine depends on the duration and the conditions of precipitation. This is more clearly illustrated by Weinland and Koch [6]. On the other hand, Bjerrum [7], who believed that he had isolated an intermediate light-green chloride, neatly classifies them on the basis of analytical data as giving reactions for 1,2 and 3 chlorine atoms.

Gapon [8] used Bjerrum's scheme in an investigation of the kinetics of hydration of chromium chloride on the basis of stepwise separation of chlorine ions. This method is not reliable.

Determination of chlorine in the green chromium chloride hexahydrate by the volumetric method at room temperature gives results corresponding to the total chlorine content. The same results are also obtained in chlorine determinations at 0°. Chlorine determination by the gravimetric method gives variable results, depending on the temperature of precipitation and on the acidification up to the limit of the equivalent for the three atoms.

On following the instructions of Bjerrum, we failed to isolate his chloride, and its existence appears to us to be unproved both from preparative and thermographic standpoints (see below). Moreover, when the dark-green chloride is pulverized, it changes to light-green; the same change occurs when dried over sulfuric acid, and two molecules of water are lost. Bjerrum suggested that his product should be dried over sulfuric acid and in vacuum.

Karyakin [9] gave a recipe for the preparation of this chloride which led to the dark-green chloride of Recoura.

In one of his papers the latter [10] describes the preparation of a brown trihydrate of chromium chloride which is not an electrolyte and to which he assigns the formula: $\left[\begin{matrix}\mathrm{Cl_3}\\ \mathrm{Cr(H_2O)_3}\end{matrix}\right]$

Pfeiffer [11] also proposed Werner's structure for this product; he obtained this complex in aqueous solution but did not isolate it in the solid state.

In the opinion of these authors, therefore, chromium chloride formed a series similar to the series of Werner and Miolatti for cobalt and platinum.

On attempting to prepare Recoura's brown compound, we actually obtained (following his instructions) a change of color of the ethereal solution to brown and isolated a small amount of solid which we were inclined to regard as a product in which part of the water had been replaced by ether and which on contact with water was reconverted into the green modification. At all events, therefore, this brown modification is not as stable as the green or violet modification.

The electrical conductivity method was used for determination of the structure of the complexes. Werner had shown that whereas the molar electrical conductivity of the grey modification is constant from the very start (350 reciprocal ohms), the electrical conductivity of the green modification rises to the magnitude of the former in the course of several hours. This instability of the green modification, at least in weak concentrations, was not clarified in the literature. Werner and Gubser [5] in one case in such solutions obtained an electrical conductivity of the order of 500 reciprocal ohms and did not give this fact the attention it deserved.

If we take into account the possibility of hydrolysis of the chloride to chromium hydroxide, then the molar electrical conductivity of such a solution may be expected to be of the order of 700 reciprocal ohms.

On measuring the electrical conductivity of 0.001 M solutions of chromium hydroxide, previously heated to 100° (i.e. solutions which may be strongly hydrolyzed), we obtained a molar electrical conductivity of the order of 680 reciprocal ohms.

In thermographic investigation of chromium chloride preparations with a straight thermocouple in an open vessel, the first halt ~~is at 84°,~~ corresponding to the melting point. Subsequently the temperature rises steadily and no halts are observed. This is evidently bound up with gradual loss of water. When the sample was heated in a vessel of the Stepanov type, i.e. under the pressure of its own vapor, apart from the melting point halt there was observed a halt at about 150°, corresponding to loss of water, and one at about 300°, marking the start of decomposition.

Thermograms obtained with a differential recorder on a Kurnakov pyrometer for the green modifications prepared by the method of Recoura and the method of Bjerrum (Figs. 1 and 2) were identical both in respect of the course of the curve and in that of the temperature halts on the curve. The first halt at 84° corresponds to the melting point of the sample; the second at 152° marks the complete removal of water.

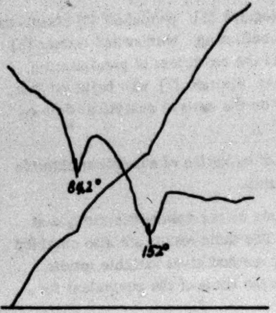


Fig. 1. Thermogram of Recoura's green chloride.

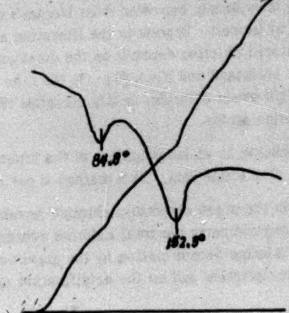


Fig. 2. Thermogram of Bjerrum's green chloride.

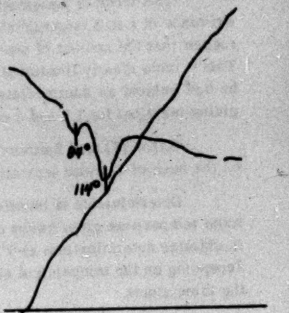


Fig. 3. Thermograms of the grey chloride.

Examination of the preparations by simple heating confirms the above observations.

When heated to 150-170°, all the water is lost, following which the weight remains constant. On heating to a higher temperature, there is observed - starting at 270-300° - a further loss in weight at the expense of chlorine; the green chloride at first then acquires a violet color, on further calcination it becomes dark-grey and then dirty-green. Chromium oxide is formed as a result of calcination. Rapid heating leads to cleavage of hydrogen chloride; slow heating results at first in loss of all the water and then in decomposition with loss of chlorine.

When moist samples are heated, yet another halt is observed on the thermogram, at 131.5°, corresponding evidently to loss of hygroscopic water.

The thermogram of the violet modification of chromium chloride hydrate gives two halts at 84 and 114° (Fig. 3).

From the structure of the isomers of the hexaaquo chromium chloride it was to be expected that, due to the different properties of the water located inside the sphere of the complex and that outside the sphere, the water would be lost at different temperatures. This was actually reflected on the thermogram.

X-ray powder diagrams, photographed at our request in a cylindrical camera of the Debye type using chromium radiation, showed identical X-ray patterns for the green modifications obtained by the methods of Recoura and Bjerrum. In both cases the X-ray diagrams were grainy. The picture is not substantially altered by grinding. These two diagrams are identical with the X-ray diagram of the anhydrous chloride which gives a normal pattern. The X-ray diagram of the grey modification is less grainy than those of green modifications and differs slightly from the latter. The X-ray diagram of the anhydrous specimen contains a large number of lines.

The concept of the so-called hydrate isomerism, which finds mention in modern textbooks [1,3] mainly on the basis of chromium chloride, appears to us to be lacking a sound foundation. It is difficult to conceive that in the system water-dissolved salt for such a relatively simple case as chromium chloride hydrate, different forms could exist in solution for a longer or shorter period of time. Up to now too little consideration has been given to the difference between the state of a substance in the solid form and that in solution, especially in water.

SUMMARY

1. Of the four modifications of chromium chloride hydrate described in the literature, only two can reliably be said to exist – the grey (often described as violet in the literature) and the green modifications.

2. The method of argentometric analysis of the aqueous solutions cannot be used as a method of distinguishing between the individual modifications.

3. Thermographic investigation did not reveal any difference between the two green modifications and between the behavior of the water in the inner and outer coordination spheres of a given modification.

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THE MECHANISM OF REDUCTION OF ACID SODIUM TUNGSTATES AND THE FORMATION OF BRONZES

S. I. Sklyarenko and L. E. Levin

Researches of a series of authors [1,2,3,4] have established that whereas the electrolysis of fused neutral sodium tungstate leads to separation of metallic tungsten at the cathode, electrolysis of acid tungstates gives tungsten bronzes.

In the present research a study was made of the mechanism of reduction of acid tungstates by metallic sodium and of the conditions of formation of tungsten bronzes.

The mechanism of reduction of acid tungstates by hydrogen was studied by V. I. Spitsyn [5]. He showed that during the first stage of the process the acid tungstate loses an atom of oxygen to form the corresponding bronze. Later the reduction proceeds in the temperature interval of 550-700° in strictly consecutive order from a less reduced to a more reduced bronze with separation of the metal: blue bronze $-Na_2W_5O_{15}[Na_2O\cdot(WO_3)_4WO_2]$; violet bronze $-Na_2W_4O_{12}[Na_2O(WO_3)_3\cdot WO_2]$; red bronze $-Na_2W_3O_9[Na_2O(WO_3)_2\cdot WO_2]$; golden-yellow bronze $-Na_2W_2O_6[Na_2O\cdot WO_3\cdot WO_2]$.

The final product of reduction is neutral tungstate and metal.

Brunner [6] prepared bronzes by fusion of neutral or acid tungstate with tungsten dioxide in absence of air according to the equation:

$$Na_2WO_4 + WO_2 = Na_2W_2O_6;\ Na_2WO_4 + WO_3 + WO_2 = Na_2W_3O_9 \text{ etc.}$$

Philipp [7] obtained bronzes by reduction of acid tungstates with tin. He also showed that by fusion of bronzes with strongly acid or neutral tungstates it is possible to obtain bronzes respectively enriched or impoverished in tungsten trioxide. This method permits transition from one bronze to another.

Spitsyn and Cherepnev [8], when investigating the electrical conductivity of fused acid sodium tungstates, came to the conclusion that these compounds dissociate in melts with formation of free tungsten trioxide. A similar conclusion may be reached on inspecting the shape of the curve of the fusion diagram of the system sodium tungstate-tungsten trioxide.

It was previously shown that the first stage of the reaction of acid tungstates with sodium is marked by reduction of the free tungsten trioxide which is always present in the melt due to dissociation of the acid tungstate. Reduction of the trioxide proceeds according to the equations:

$$WO_3 + 6Na = 3Na_2O + W, \qquad (1)$$

$$3Na_2O + 3WO_3 = 3Na_2WO_4 \qquad (2)$$

or overall:

$$4WO_3 + 6Na = 3Na_2WO_4 + W. \qquad (3)$$

Reaction (1) is a reaction of the eighth order and it is most unlikely that it takes place in one step. A more reasonable assumption is that reaction (1) proceeds through certain intermediate stages the first of which consists in reduction of tungsten trioxide to dioxide according to the equation:

$$2Na + WO_3 = Na_2O + WO_2. \qquad (4)$$

Sodium oxide reacts further with excess of trioxide:

$$Na_2O + WO_3 = Na_2WO_4. \qquad (5)$$

The over-all reaction of the first step of the process will proceed according to the equation:

$$2Na + 2WO_3 = Na_2WO_4 + WO_2. \qquad (6)$$

In suitable conditions the formed tungsten dioxide is further reduced to tungsten. We might assume that the further reduction proceeds according to the equation:

$$4Na + WO_2 = 2Na_2O + W. \qquad (7)$$

But this is a reaction of the fifth order, and its probability is likewise very low. Evidently the reduction of the dioxide to tungsten proceeds by another route.

Friderich and Sittig [9], when investigating the properties of lower oxides of some metals, established that calcination in vacuum of tungsten dioxide at 1500-1600° leads to decomposition into metallic tungsten and tungsten trioxide; the latter sublimed and was deposited on the cold part of the apparatus. On the other hand, when a pelleted mixture of the trioxide and metallic tungsten was calcined at 1000° in the absence of air, tungsten dioxide was obtained. The authors did not draw any conclusions whatever from these experiments. We may infer that a reversible reaction took place:

$$3WO_2 \rightleftarrows 2WO_3 + W. \qquad (8)$$

It is interesting to note that the thermal effect of this reaction, calculated from thermochemical data [10] at 18°, is 0.1 kcal, i.e. substantially equal to zero.

In normal conditions the equilibrium of reaction (8) is evidently shifted far to the left. If, however, the trioxide could be removed from the sphere of reaction, then the equilibrium would be shifted to the right and reaction (8) would proceed to completion with formation of tungsten. In the experiments of Friderich and Sittig, this was accomplished by using high temperatures (1500-1600°) at which the trioxide sublimed and left the sphere of reaction.

A similar case of an equilibrium shift occurs in the reaction of tungsten dioxide with hydrogen chloride. V. I. Spitsyn and L. I. Kashtanov [11] found that at 400° the following reaction takes place when a stream of dry HCl is passed over tungsten dioxide:

$$3WO_2 + 4HCl = 2WO_2Cl_2 + 2H_2O + W. \qquad (9)$$

Assuming that reaction (8) is valid and allowing for the volatility of tungsten oxychloride, we may propose the following scheme for reaction (9):

$$\begin{aligned} 3WO_2 &\longrightarrow 2WO_3 + W, \\ 2WO_3 + 4HCl &\longrightarrow 2WO_2Cl_2 + 2H_2O. \end{aligned} \qquad (9')$$

For the purpose of experimental verification of the possibility of displacement of the equilibrium of reaction (8), tungsten dioxide was heated in admixture with substances capable of combining with the trioxide formed in reaction (8), thereby shifting the equilibrium to the right. The substances selected had basic properties and were consequently able to combine with tungsten trioxide: sodium pyrophosphate, borax and calcium oxide. The tungsten dioxide required for the experiments was prepared by the method of van-Liempt [12] and G. A. Meerson [13].

Tungsten trioxide in a porcelain boat was reduced in a tube furnace at 850° for 3 hours with purified hydrogen which had been previously saturated with water vapor by passing it through two wash bottles containing water at 85-87°.

Reduction gave a brown powder of tungsten dioxide; the value of x in WO_x was calculated from the analytical data. We selected only those specimens of dioxide in which the value of x was not less than 2, since otherwise the dioxide would have been slightly over-reduced. A small under-reduction was of no consequence.

Sodium pyrophosphate, borax and calcium oxide were prepared in the pure form by the methods described in the literature.

Tungsten dioxide and one of the above-mentioned substances were mixed in a definite ratio and charged into a porcelain crucible; the crucible was placed in an iron bomb which was screwed tight with a cover, through an opening in which was led a porcelain tube for passage of a stream of dry, oxygen-free nitrogen.

The bomb, with crucible in position, was first carefully purged with nitrogen and then inserted in a furnace at red heat and kept there for an hour in a current of nitrogen. It was then cooled in a nitrogen stream. After an experiment the melt was lixiviated with water and the reaction products were collected and analyzed. Experimental results are set forth in Table 1.

All the three compounds gave pure metallic tungsten when heated with tungsten dioxide. The yield of tungsten was calculated from reaction (8).

Since none of the substances used is a reducing agent, the formation of metal can only be explained by reaction (8).

TABLE 1

Expt. No.	Added substance	Amount		Molar ratio of added substance to WO_2	Analyzed comp. of WO_2	Reaction temp.	Comp. of obtained product	Yield of tungsten	
		of added substance (in g)	of WO_3 (g)					in % of theoretical	purity of W by analysis (in %)
1	Sodium pyrophosphate	22.0	3.45	5.17:1	$WO_{2.00}$	1000	Metallic tungsten	72.5	99.2
2	Borax	32.7	2.42	14.5:1	$WO_{2.09}$	920	Ditto	30.6	99.3
3	Calcium oxide . .	2.29	4.41	0.5:1	$WO_{2.08}$	930	"	35.0	99.9

The over-all reaction between the dioxide and the stated compounds may be represented by the following equations:

$$3WO_2 + 2Na_4P_2O_7 = 2Na_2WO_4 + 4NaPO_3 + W, \quad (10)$$

$$3WO_2 + 4Na_2B_4O_7 = 2Na_2WO_4 + 2(Na_2O \cdot 4B_2O_3) + W, \quad (11)$$

$$3WO_2 + 2CaO = 2CaWO_4 + W. \quad (12)$$

At the basis of reactions (10), (11) and (12) are the reactions:

$$Na_4P_2O_7 + WO_3 = Na_2WO_4 + 2NaPO_3,$$

$$2Na_2B_4O_7 + WO_3 = Na_2WO_4 + Na_2O \cdot 4B_2O_3,$$

$$CaO + WO_3 = CaWO_4,$$

of which the over-all expression is (8).

The results of the experiments are sufficiently convincing evidence of the occurrence of reaction (8).

Consequently the reduction of acid tungstates by metallic sodium may be considered to proceed in the following manner. The first stage in reduction of the acid tungstate is reduction of tungsten trioxide with formation of dioxide according to equations (4) and (5). The further course of the process depends on the state of equilibrium of reaction (8). The state of this equilibrium in the given conditions is determined by the properties of the medium. If the medium is basic, then the tungsten trioxide is bound and the equilibrium of (8) is shifted to the right in the direction of formation of metal. In an acid medium the equilibrium is shifted to the left and metal is not isolated.

When acid sodium tungstates are reduced, there will correspond to the basic or acidic character of the medium, respectively, an excess or deficiency of the sodium necessary for reduction of the whole of the free (excess) tungsten trioxide to metal. Let us consider this case more closely.

1. Excess of sodium. The reduction reaction proceeds in the following manner:

$$3WO_3 + 6Na = 3WO_2 + 3Na_2O,$$

$$3WO_2 = 2WO_3 + W,$$

$$2WO_3 + 2Na_2O = 2Na_2WO_4.$$

The residue of sodium oxide is bound by free trioxide:

$$Na_2O + WO_3 = Na_2WO_4.$$

The sum of these reactions gives equation (3).

The reaction leads to separation of metallic tungsten.

2. Deficiency of sodium. There is an excess of tungsten trioxide in the medium. At the start, as in the preceding case, tungsten dioxide is formed, while sodium oxide is bound by excess of tungsten trioxide.

But due to the excess of trioxide, equation (8) will be shifted to the left. Hence the tungsten dioxide will not be decomposed with formation of tungsten, but dioxide will accumulate.

Tungsten dioxide is bound to form a bronze with sodium tungstate in accordance with Brunner's reaction:

$$Na_2WO_4 + WO_2 = Na_2W_2O_6 \quad (13)$$

and then, in presence of excess trioxide:

$$Na_2W_2O_6 + WO_3 = Na_2W_3O_9 \qquad (14)$$
$$Na_2W_3O_9 + WO_3 = Na_2W_4O_{12}. \qquad (15)$$

Consequently, when acid tungstates are reduced with a deficiency of sodium, bronzes are certain to be formed and they are consequently products of incomplete reduction of acid tungstates.

V. I. Spitsyn showed that when acid tungstates are reduced with hydrogen the degree of reduction of the obtained bronzes increases with increasing amount of reducing agent. The bronzes may be arranged in the following order of increasing degree of reduction: Blue, violet, red, golden yellow. Similarly in reduction with sodium the degree of reduction must increase with increasing amount of sodium.

In our preceding paper we introduced the concept of the critical value of the sodium amount. By this term is to be understood the ratio (in %) of(on the one hand)the amount of sodium necessary for reduction of all the free trioxide to tungsten and neutral tungstate to (on the other) the amount of sodium necessary for complete reduction both of the trioxide and of all the neutral tungstate according to the equation:

$$Na_2WO_4 + 6Na = 4Na_2O + W$$
$$\text{and } WO_3 + 6Na = 3Na_2O + W.$$

If the amount of sodium used for reduction is less than the critical value, then an excess of trioxide remains and bronzes must be formed. Consequently the critical value may be regarded as a limiting value below which bronzes are obtained and above which tungsten is obtained.

The literature does not contain any data about the preparation of bronzes with the help of metallic sodium. It was therefore of interest to undertake a series of experiments on the reduction of acid tungstates by sodium. Reduction was accomplished in an iron bomb at 800-900°. After an experiment, the reaction mass was lixiviated with water and the character of the products was determined. The experimental results are set forth in Table 2. The amount of sodium (in %) was calculated in relation to the theoretical amount of sodium necessary for complete reduction of all the tungstate. In the sixth column are the critical values of sodium calculated for tungstate of the given composition.

The experimental results show that reduction of acid tungstates with an inadequate amount of sodium leads to tungsten dioxide and bronzes. The limiting character of the critical value of sodium is here very clearly illustrated. In all cases, when the amount of sodium even very slightly exceeds the critical value, metal is formed. If the amount of sodium is below this critical value, we obtain bronzes, tungsten dioxide or a mixture of these with metal.

When there is little tungsten trioxide in the starting mixture, reduction gives mainly dioxide. When there is a large proportion of trioxide we obtain bronzes. The closer the amount of sodium approaches to the critical value, the higher the degree of reduction and, conversely, with decreasing amount of sodium the degree of reduction correspondingly decreases. In this case we observe the same sequence as was established by V. I. Spitsyn for reduction of acid tungstates with hydrogen.

Such a sequence in the reduction of acid tungstates is fully explained by the above scheme. With an excess of trioxide the equilibrium of equation (8) is shifted in the direction of formation of dioxide which, as already shown, combines with tungstates to form bronzes in accordance with equations (13) to (15).

There is every reason for assuming that these reactions are reversible. Brunner showed that bronzes are capable of decomposing according to a reversible reaction, for example:

$$3Na_2W_2O_6 \rightleftarrows 3Na_2WO_4 + 2WO_3 + W.$$

But the last two terms of this equation are in equilibrium with WO_2 according to reaction (8).

On calculating the second equation from the first, we arrive at equation (13a) in analogy with equation (13):

$$3Na_2W_2O_6 \rightleftarrows 3Na_2WO_4 + 3WO_2. \qquad (13a)$$

On the other hand, as already indicated above, we know from Philipp's work that bronzes are capable of enrichment or impoverishment in tungsten trioxide by fusing them with salts containing an excess or deficiency of trioxide. Consequently equations of the type of (14), (15), etc. are likewise reversible.

TABLE 2

Expt. No.	Composition	Amount (in g)	Amount of Na (% of theory)	Crit. val. of Na (%)	Reaction products
1	Eutectic: Na_2WO_4 80 mole-%. WO_3 20 mole %.	22.2	2.02	5.0	Tungsten dioxide
2	Ditto	25.0	2.08	5.0	Tungsten dioxide
3	"	24.0	4.0	5.0	Mixture of tungsten dioxide and tungsten
4	"	14.5	5.2	5.0	Tungsten
5	"	25.0	6.3	5.0	Tungsten
6	Ditungstate $Na_2W_2O_7$	20.0	2.95	12.5	Mixture of tungsten dioxide and tungsten bronze
7	Ditto	20.0	6.2	12.5	Tungsten dioxide
8	"	15.0	12.7	12.5	Tungsten
9	Paratungstate $5Na_2O \cdot 12WO_3$	20.0	1.96	14.58	Mixture of red and violet bronzes
10	Ditto	20.0	4.2	14.58	Blue bronze (640°)
11	"	20.0	12.0	14.58	Golden-yellow bronze
12	"	25.0	17.6	14.58	Tungsten
13	"	20.0	26.5	14.58	Tungsten

On this basis we may conclude that reactions (8), (13), (14), (15), etc. form a group of closely linked reactions.

$$\begin{array}{cc|c|cr}
\longrightarrow & & 2WO_3 + W \rightleftarrows 3WO_2 & \uparrow & (8)\\
\text{Decrease of} & & Na_2WO_4 + WO_3 \rightleftarrows Na_2W_2O_6 & \text{Increase of} & (13)\\
\text{Na} & & Na_2W_2O_6 + WO_3 \rightleftarrows Na_2W_3O_9 & \text{Na} & (14)\\
 & \downarrow & Na_2W_3O_9 + WO_3 \rightleftarrows Na_2W_4O_{12} & \longleftarrow & (15)
\end{array}$$

With decreasing amount of sodium taken for the reduction, the amount of residual trioxide increases and the equilibrium of all the above reactions will be shifted to the right and downward, i.e. in the direction of formation of less reduced bronzes. With progressive increase of the sodium amount, the amount of residual trioxide will decline and the equilibrium of the whole group of reactions will be shifted to the left and upward. Hence we begin to get an increasing amount of dioxide — the last stage of reduction on the route to tungsten. As soon as the amount of sodium exceeds the critical amount, the latter stage of reduction will be attained and formation of tungsten will commence.

Consequently with gradual increase in the content of sodium and correspondingly gradual decrease in the quantity of trioxide, the reaction products pass successively through all the stages of reduction on the way to metal. The whole group of these reactions constitutes a unified complex in which each individual reaction is closely linked with all the others. This also accounts for the fact that usually we always obtain a mixture of bronzes, the separation of which into pure constituents is a rather complex problem when sufficient excess of trioxide is present.

SUMMARY

1. A study was made of the mechanism of reduction of acid sodium tungstates by metallic sodium. It was shown that this reaction proceeds in two stages. Tungsten dioxide is formed in the first stage. The second stage depends on the character of the medium and is governed by the state of equilibrium of the reversible reaction:

$$3WO_2 \rightleftarrows 2WO_3 + W.$$

2. It was established that when acid tungstates are reduced by sodium, the character of the reaction products depends on the degree of acidity of the medium. If the amount of sodium taken for the reduction is sufficient to impart a basic character to the medium, then the equilibrium of equation (8) will be shifted to the right, in the direction of formation of metallic tungsten. When there is a deficiency of sodium and the medium has an acidic reaction, then equation (8) is shifted to the left, in the direction of formation of tungsten dioxide.

3. The possibility was demonstrated of obtaining tungsten bronzes by the action of metallic sodium on acid sodium tungstates. The conditions of formation and the mechanism of formation of bronzes were clarified. It was established that the character of the resultant bronzes depends on the acidity of the medium and is governed by the state of equilibrium of a group of reversible reactions which are closely linked with one another.

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RECIPROCAL SYSTEM OF THE ADIAGONAL-BELT EUTECTIC TYPE OF METAPHOSPHATES AND SULFATES OF LITHIUM AND POTASSIUM

A. G. Bergman and M. L. Sholokhovich

The presence of well-defined complexes in systems may completely alter the chemism anticipated on the basis of the conventionally calculated thermal effect of the exchange reaction [1]. The decisive factor governing the direction of a reaction is the ratio of the heats of the exchange reaction and of the complex-forming reaction. In systems containing one complex compound, triangulation on three phase triangles may proceed in two diametrically opposed directions.

1) In the case of predominance of the heat of the reaction of exchange decomposition, the main triangular section is the diagonal (diagonal type; Fig. 1).

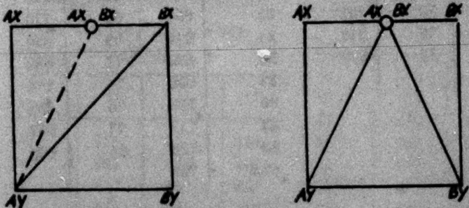
2) But when the heat of the complex-forming reaction predominates, triangulation is effected by a secant starting from the representative point of the double compound (diagonal type, in the triangulation of which none of the diagonals takes part; Fig. 2).

It appeared to be of very great interest to investigate systems containing well-defined complexes at opposite sides and a continuous series of solid solutions on the remaining two sides. We shall consider three types:

1) The reciprocal systems consist of three series of continuous solid solutions; the systems are divided into two tetragons with a single secant, starting from both representative points of the compounds; the formed tetragons are not subjected to further triangulation (Fig. 3). Examples: Ca, Sr || F, Cl [2]; Ba, Sr || F, Cl [3].

2) The sharp displacement of the exchange decomposition causes a break in the continuous solid solutions and division of the stable diagonal into two phase triangles (Fig. 4). Example: K, Na || SO_4, F [4].

3) A special "belt" eutectic type is the reciprocal system (investigated by us) of the metaphosphates and sulfates of lithium and potassium Li, K || SO_4, PO_3 (Figs. 5 and 13), described in detail in the concluding part of the paper. Its special characteristic is the presence in the system of a more stable section starting from the representative points of the complexes lying on opposite sides of the system. These sections of the system are divided into two tetragons which in turn are subjected to triangulation into two phase triangles. None of the diagonals in the triangulated system participates (Fig. 5). Neither the components nor the compounds form solid solutions with one another.



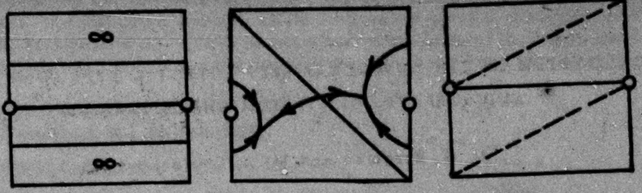
Figs. 1 and 2. Main types of diagonal systems with one complex component AX · BX on the sides.

EXPERIMENTAL

The investigation was carried out by the visual-polythermic method of fusion. The crucible was of platinum. The thermocouple was made of Pt–Pt/Rh alloy and incorporated an extremely sensitive multiscale millivoltmeter. The liquidus curves were determined from the temperatures of disappearance of crystals due to persistent vitrification of the melts enriched with lithium metaphosphate. Calculations were made with equimolar percentages. Lithium metaphosphate was prepared by fusion of chemically pure monoammonium phosphate with lithium carbonate. Melting points of salts: KPO_3 —798°; $LiPO_3$ —634°; Li_2SO_4 —860°; K_2SO_4 —1069°. Part of the tabulated experimental material has been omitted to cut down the length of this paper.

Binary Systems

1) $(KPO_3)_3$—K_2SO_4 (Table 1, Fig. 6). This system is here investigated for the first time. There is a eutectic at 22 % K_2SO_4 and 718°.



Figs. 3, 4 and 5. Main types of reciprocal systems containing one complex compound at each of two opposing sides and a continuous series of solid solutions at the other opposing sides.

TABLE 1

% K_2SO_4	t°	% K_2SO_4	t°
2	790	40	820
4	782	45	852
6	776	50	874
10	766	54	888
13	758	60	908
16	752	64	926
20	736	70	941
21	728	75	961
23	728		
26	744		
30	764		
35	790		

TABLE 2

% $(LiPO_3)_2$	t°	% $(LiPO_3)_2$	t°
5	806	27.5	610
10	744	30	598
15	692	32.5	580
20	664	35	570
22.5	644		
25	628		

TABLE 3

% $(LiPO_3)_2$	t°	% $(LiPO_3)_2$	t°
4	774	36	536
8	744	40	544
12	720	42.5	551
16	694	50	562
20	866	55	550
24	641	60	532
28	609	65	528
32	582	70	548
		75	566

TABLE 4

% Li_2SO_4	t°	% Li_2SO_4	t°
3	774	45	564
6	747	50	578
9	720	55	582
13	682	60	578
16	647	65	574
20	612	70	554
23	590	75	536
25	574	78	520
27.5	568	82.5	524
30	564	85	540
33	562	90	569
36	550	92.5	620
40	530	95	700
41	540		

TABLE 5

% K_2SO_4	t°	% K_2SO_4	t°
26	538	80.	582
27.5	528	55	605
29	520	56.5	608
30.5	504	58	613
32	487	60	620
33.5	468	61.5	642
35	470	63	666
36.5	478	65	694
38	487	70	751
41	508	75	810
44	528	80	870
47	554		

TABLE 6

Section 1 [50% Li_2SO_4 + 50% K_2SO_4] → → $(KPO_3)_2$

% $(KPO_3)_2$	t°	% $(KPO_3)_2$	t°
0	736	51	720
5	718	54	720
10	700	57	720
15	680	60	718
17.5	670	63	714
20	658	66	710
21	674	69	694
24	690	71	682
27	698	74	674
30	706	75	654
33	713	77	682
39	720	80	698
47.5	720		

2) Li_2SO_4–$(LiPO_3)_2$ (Table 2, Fig. 7). Investigated to 70% $(LiPO_3)_2$; further investigation hindered by vitrification. Eutectic at 47.5% $(LiPO_3)_2$ and 508°. Transformation point of the α-modification of Li_2SO_4 into the β-modification at 574° and 33.5% $(LiPO_3)_2$.

3) $(KPO_3)_2$–$(LiPO_3)_2$ (Table 3, Fig. 7). Investigated for the first time. A compound $LiPO_3 \cdot KPO_3$, melting at 562°, is formed. The eutectics correspond to: E_1 – 37% $(LiPO_3)_2$ and 528°; E_2 – 64% $(LiPO_3)_2$ and 518°.

TABLE 7

Section II
[50% Li_2SO_4 + 50% K_2SO_4] $\longrightarrow$
$\longrightarrow$ $Li_2(PO_3)_2$

% $(LiPO_3)_2$	t°	% $(LiPO_3)_2$	t°
0	736	40	554
5	710	45	534
10	690	50	506
15	670	52	494
20	648	54	483
25	624	55	505
30	604	57.5	520
35	580	60	530

TABLE 8

Section III
[50% $(KPO_3)_2$ + 50% $(LiPO_3)_2$] $\longrightarrow$
$\longrightarrow$ K_2SO_4

% K_2SO_4	t°	% K_2SO_4	t°
0	562	25	510
5	543	28	532
9	528	32	566
12	516	35	590
16	504	40	636
17.5	494	45	682
20	500	50	720
22.5	506		

TABLE 9

Section IV
[30% $(LiPO_3)_2$ + 70% Li_2SO_4] $\longrightarrow$
$\longrightarrow$ $(KPO_3)_2$

% $(KPO_3)_2$	t°	% $(KPO_3)_2$	t°
0	588	35	524
5	550	40	520
10	504	45	500
13	476	50	470
15	458	52	454
17	452	54	474
18	462	56	486
19	470	60	512
20	473	62.5	528
21	478	65	546
23	492	70	600
25	504	75	646
30	520		

TABLE 10

Section V [20% $(LiPO_3)_2$ + 80% Li_2SO_4] $\longrightarrow$ $K_2(PO_3)_2$

% $(KPO_3)_2$	t°	% $(KPO_3)_2$	t°
0	664	45	540
3	606	50	520
5	564	55	508
10	538	56	500
13	510	57	490
15	482	60	512
17.5	467	62.5	526
20	484	65	536
25	528	70	540
30	550	75	600
35	550	80	660
40	548		

TABLE 11

Section VI [90% Li_2SO_4 + 10% K_2SO_4] $\longrightarrow$ $(LiPO_3)_2$

% $(LiPO_3)_2$	t°	% $(LiPO_3)_2$	t°
20	566	46	496
25	552	48.3	520
30	538	51.7	534
33	530	55	554
36	524	58.9	566
39	508	64.8	582
42	496	72	601
45	484		

TABLE 12

Section VII [80% Li_2SO_4 + 20% K_2SO_4] $\longrightarrow$ $Li_2(PO_3)_2$

% $(LiPO_3)_2$	t°	% $(LiPO_3)_2$	t°
0	539	45	491
5	530	48	504
10	524	51	520
20	510	54	536
25	502	57	545
30	494	60	560
33	487	63	572
36	478	66	582
39	476	69	591
42	470	72	600

TABLE 13

Section VIII [65% Li_2SO_4 + 35% K_2SO_4] $\longrightarrow$ $Li_2(PO_3)_2$

% $(LiPO_3)_2$	t°	% $(LiPO_3)_2$	t°
0	674	35	494
10	642	37.5	480
15	617	40	462
20	586	43	460
25	558	45	484
30	528	50	500

TABLE 14

Section IX A [50% Li_2SO_4 + 50% K_2SO_4] $\rightarrow$ B [50% $(KPO_3)_2$ + 50% $(LiPO_3)_2$]

% B	t°	% B	t°
0	736	55	560
10	710	60	536
15	698	65	504
20	682	70	496
25	670	75	514
30	658	80	523
35	642	85	534
40	624	90	546
45	608	95	558
50	586	100	562

It was extremely interesting to observe a marked fall in viscosity of lithium metaphosphate under the action of the added potassium metaphosphate in spite of the formation of a double compound and a fall in melting point. The molecular structure of this compound is evidently less complex than that of lithium metaphosphate.

4) Li_2SO_4–K_2SO_4. Repeatedly investigated [5]. Forms a compound $Li_2SO_4 \cdot K_2SO_4$, melting, according to our determinations, at 736°.* Eutectics at: E_1 – 39% Li_2SO_4 and 712°; E_2 – 80% Li_2SO_4 and 535°.

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* A. E. Bergman and E. K. Akopov later established the existence of the compound $2Li_2SO_4 \cdot K_2SO_4$, melting incongruently at 573°; consequently on the diagram of the reciprocal system from the 573° point of the lateral binary system the limit of the crystallization field is shown by a broken curve (Fig. 9). The field of this compound obviously terminates inside the system.

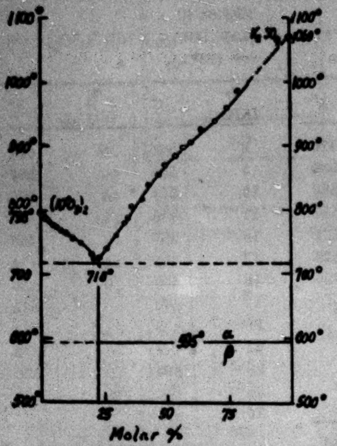

Fig. 6. Fusibility of the system $(KPO_3)_2-K_2SO_4$.

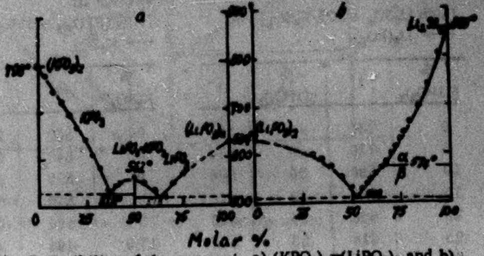

Fig. 7. Fusibility of the systems: a) $(KPO_3)_2-(LiPO_3)_2$ and b) $(LiPO_3)_2-Li_2SO_4$.

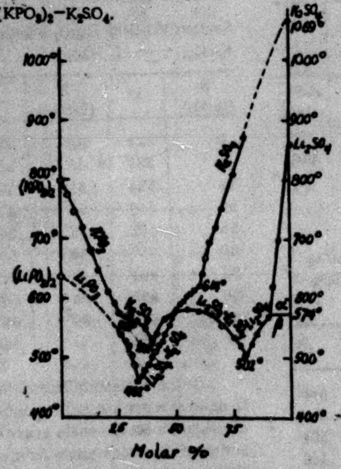

Fig. 8. Diagonal sections of the reciprocal system Li, K ‖ SO_4, PO_3.

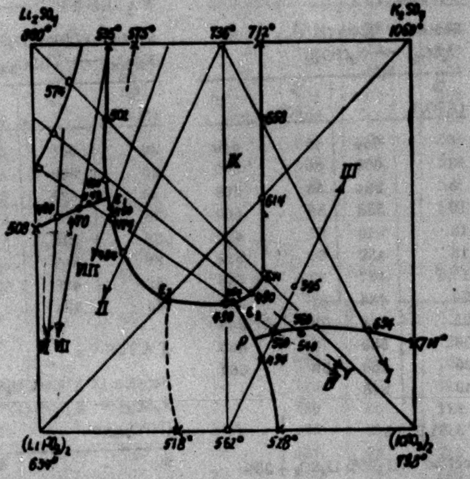
Li₂SO₄
860°
595°
575°
736°
712°
K₂SO₄
1069°
574
502
658
614
508
470
II
III
VIII
VII
I
IX
E₁
E₂
E₃
P
430
596
569
540
534
716°
(LiPO₃)₂
634°
518°
561°
528°
(KPO₃)₂
798°

Fig. 9. Chart of internal sections through the reciprocal system Li, K ‖ SO_4, PO_3.

Diagonal Sections

None of the diagonal sections is stable and both intersect the products of double decomposition.

1. $(KPO_3)_2-Li_2SO_4$ (Table 4, Fig. 8). The liquidus curve comprises branches of crystallization of potassium metaphosphate, the double sulfate of lithium and potassium, and the α- and β-modifications of lithium sulfate.

Points of intersection of the branches: 1) 26% Li_2SO_4 and 569°; 2) 40.5% Li_2SO_4 and 524°; 3) 55% Li_2SO_4 and 582°; 4) 80.5% Li_2SO_4 and 502°. Transformation points of the α- and β-modifications of Li_2SO_4 at 91% Li_2SO_4 and 574°.

2. Section $Li_2(PO_3)_2-K_2SO_4$ (Table 5, Fig. 8). The section intersects the field of crystallization of lithium metaphosphate, the double sulfate of lithium and potassium, and potassium sulfate. There is a slight inflection on the $Li_2SO_4 \cdot K_2SO_4$ branch at 50% K_2SO_4 whose significance we have not yet established.

Points of intersection of the branches: 1) 33% K_2SO_4 and 462°; 2) 60% K_2SO_4 and 614°.

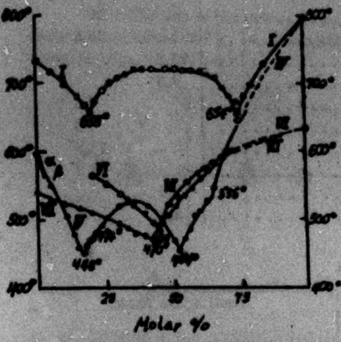

Fig. 10. Internal sections through the system:

I – 50% K_2SO_4 } 50% Li_2SO_4 } → $[KPO_3]_2$;

VI – 90% Li_2SO_4 } 10% K_2SO_4 } → $[LiPO_3]_2$;

IV – 30% $Li_2[PO_3]_2$ } 70% Li_2SO_4 } → $[KPO_3]_2$;

VII – 80% Li_2SO_4 } 20% K_2SO_4 } → $[LiPO_3]_2$.

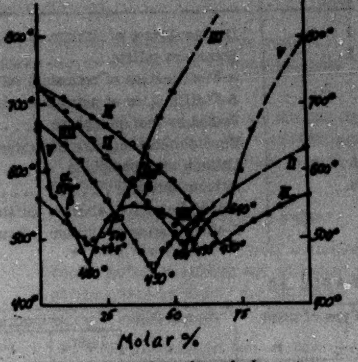

Fig. 11. Internal sections through the system:

II – 50% K_2SO_4 } 50% Li_2SO_4 } → $[LiPO_3]_2$;

IX – 50% Li_2SO_4 } 50% K_2SO_4 } → { 50% $K_2[PO_3]_2$ 50% $[LiPO_3]_2$

III – 50% $K_2[PO_3]_2$ } 50% $Li_2[PO_3]_2$ } → K_2SO_4;

V – 20% $Li_2[PO_3]_2$ } 80% Li_2SO_4 } → $[KPO_3]_2$;

VIII – 65% Li_2SO_4 } 35% K_2SO_4 } → $[LiPO_3]_3$

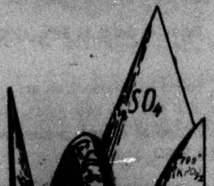
SO₄
LiPO₃·KPO₃

Fig. 12. Spatial diagram of the reciprocal system Li, K ‖ SO_4, PO_3.

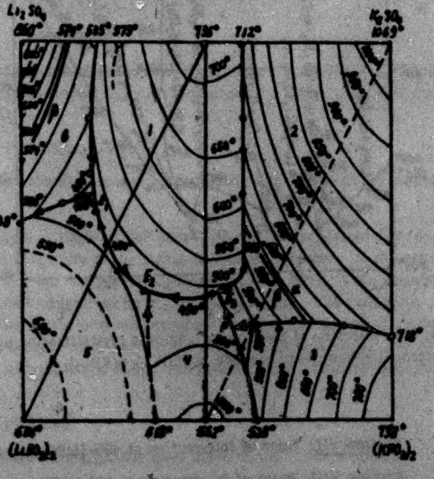
Li₂SO₄
860°
574°
585°
575°
735°
712°
K₂SO₄
1069°
1
2
3
4
5
6
E₂
700°
650°
600°
550°
500°
506°
715°
618°
618°
552°
528°
798°
(LiPO₃)₂
(KPO₃)₂

Fig. 13. Projection of the spatial diagram of the system on to the square of composition. 1) $Li_2SO_4 \cdot K_2SO_4$ field; 2) K_2SO_4 field; 3) KPO_3 field; 4) $LiPO_3 \cdot KPO_3$ field; 5) $LiPO_3$ field; 6) Li_2SO_4 field. E_1) 440°; E_2) 460°; E_3) 453; P) 474.

TABLE 15 (Fig. 13)

No. of field	Field of crystallization	Area (in %)	
1	Double sulfate of lithium and potassium		26
2	Potassium sulfate		30.5
	α-Modification of potassium sulfate	27.9	
	β-Modification of potassium sulfate	2.6	
3	Potassium metaphosphate		9.8
4	Double metaphosphate of lithium and potassium		7.9
5	Lithium metaphosphate		17.5
6	Lithium sulfate		8.3
	α-Modification of lithium sulfate	2.5	
	β-Modification of lithium sulfate	5.8	

TABLE 16

Type of point		Temperature	Composition (mole %)			Equilibrium phases
			Li_2SO_4	$(LiPO_3)_2$	$(KPO_3)_2$	
Eutectic	E_1	440	60	20.5	19.5	Li_2SO_4; $LiPO_3$; $Li_2SO_4 \cdot K_2SO_4$
	E_2	460	33.5	32.5	34	$LiPO_3$; $LiPO_3 \cdot KPO_3$; $Li_2SO_4 \cdot K_2SO_4$
	E_3	453	34	13	53	$LiPO_3 \cdot KPO_3$; K_2SO_4; $Li_2SO_4 \cdot K_2SO_4$
Transition P		474	24	19	57	$LiPO_3 \cdot KPO_3$; KPO_3; K_2SO_4

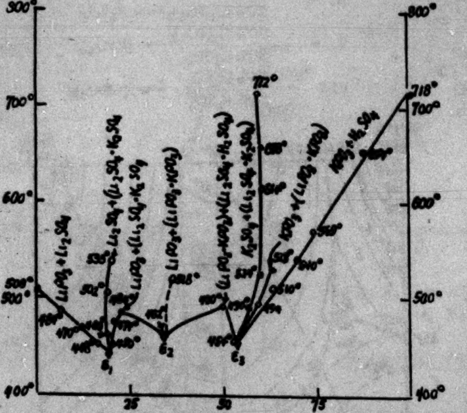

Fig. 14. Projection of the lines of common crystallization of the reciprocal system on to the side of $(LiPO_3)_2$–$(KPO_3)_2$.

Internal Sections Through the System (Fig. 9-11; Tables 6-14)

Section I. Points of intersection at: 1) 20% K_2SO_4 and 658°; 2) 75% K_2SO_4 and 654°.

Section II. Eutectic point at 54% $(LiPO_3)_2$ and 484°.

Section III. Points of intersection at: 1) 17.5% K_2SO_4 and 494°, 2) 25% K_2SO_4 and 510°. Transformation of α- and β-modifications of K_2SO_4 at 37% K_2SO_4 and 595°.

Section IV. Intersection points at: 1) 16% $(KPO_3)_2$ and 448°; 2) 21% $(KPO_3)_2$ and 474°; 3) 52% $(KPO_3)_2$ and 454°; 4) 64.5% $(KPO_3)_2$ and 536°.

Section V. Points of intersection at: 1) 18% $(KPO_3)_2$ and 460°; 2) 57% $(KPO_3)_2$ and 490°: 3) 70% $(KPO_3)_2$ and 540°. Transformation of α- and β-modifications of Li_2SO_4 at 4.5% $(KPO_3)_2$ and 574°.

Section VI. Point of intersection at 45% $(LiPO_3)_2$ and 470°.

Section VII. Point of intersection at 42% $(LiPO_3)_2$ and 470°.

Section VIII. Point of intersection at 42% $(LiPO_3)_2$ and 450°.

Section IX. Eutectic point at 67% $(LiPO_3)_2 \cdot (KPO_3)_2$ and 490°.

Spatial Diagram of the Reciprocal System (Figs. 12 and 13)

The isotherms in the lithium metaphosphate field are plotted with a broken line because here the field of vitrification was only partially investigated due to the experimental difficulty.

The projection of the curves of common crystallization on to the side of the square of the reciprocal system is represented in Fig. 14. The system contains three ternary eutectics and one ternary transition point (Table 16, Figs. 13 and 14).

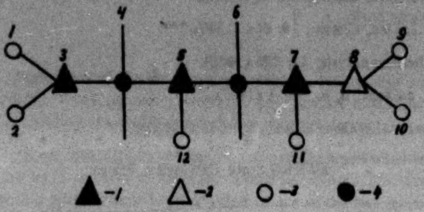

Fig. 15. Scheme of the crystallization field of the reciprocal system. 1) Ternary eutectic point (E_1, E_2, E_3); 2) ternary transition point (P); 3) binary eutectic point; 4) inflection point.

Sections II and IX are the sole stable sections of the system; they bear the character of simple binary systems whose eutectic points are turning points.

Section IX is the most stable*:

1) The fields of crystallization of the double sulfate of lithium and potassium are characterized by sharply defined ridges arranged along the given section.

2) The eutectic temperature of 490° of section IX is higher than the eutectic temperature (484°) of section II.

Fig. 15 is a diagram of the field of crystallization of the system: 1) 535°; 2) 508°; 3) 440°; 4) 484°; 5) 460°; 6) 490°; 7) 453°; 8) 474°; 9) 718°; 10) 528°; 11) 712°; 12) 518°.

Due to the absence of data for the heats of formation of $LiPO_3$ and KPO_3, it is impossible to calculate the arbitrary thermochemical effect of the double decomposition reaction; clearly it is very small, as could be determined from the fusion diagram. In both of the following equations the reaction between the starting components leads to formation of both of the double salts — of the components $Li_2SO_4 \cdot K_2SO_4$ and $LiPO_3 \cdot KPO_3$.

$$2Li_2SO_4 + 2(KPO_3)_2 \longrightarrow Li_2SO_4 \cdot K_2SO_4 + (LiPO_3)_2 \cdot (KPO_3)_2,$$

$$2(LiPO_3)_2 + K_2SO_4 \longrightarrow Li_2SO_4 \cdot K_2SO_4 + (LiPO_3)_2 \cdot (KPO_3)_2.$$

If the heat of the double decomposition reaction was higher than the heats of formation of the complexes, then reduction of both complexes should result in their decomposition with formation of a stable pair of components, as happens, for example, in the system Na, K || F, SO_4 [4]:

$$Na_2SO_4 \cdot NaF + 2K_2SO_4 \cdot KF \longrightarrow 3NaF + K_2SO_4,$$

in which the conventional thermochemical effect of the double decomposition reaction is 6.23 kcal per equivalent in the direction of the stable pair $Na_2F_2 - K_2SO_4$.

Consequently the fields of both of the compounds $Na_2SO_4 \cdot NaF$ and $K_2SO_4 \cdot KF$ are separated from each other by the stable diagonal and by the fields of crystallizations of the stable pair of components. In the system that we have investigated, however, the fields of both of the complexes $Li_2SO_4 \cdot K_2SO_4$ and $LiPO_3 \cdot KPO_3$ diverge to form a transverse belt which separates the components capable of entering into exchange. The transverse section of $Li_2SO_4 \cdot K_2SO_4 - Li_2(PO_3)_2 \cdot K_2(PO_3)_2$ divides the square into two tetragons which are subjected to secondary triangulation. The results of this investigation would be still more interesting if determinations were made of the heats of formation of metaphosphates of lithium and potassium and of the compound $LiPO_3 \cdot KPO_3$; the heat of formation of $Li_2SO_4 \cdot K_2SO_4$ has been determined [6].

SUMMARY

1. Using the visual-polythermic method of fusion, investigations were made of the liquidus surface of the binary systems

$$K_2SO_4 - K_2(PO_3)_2;\ Li_2SO_4 - Li_2(PO_3)_2;\ K_2(PO_3)_2 - Li_2(PO_3)_2$$

and of the surface of crystallization of the reciprocal system Li, K || SO_4, PO_3.

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* In Fig. 11 the stable sections are the dense, continuous curves; the unstable ones are indicated by broken curves.

2. The surface of crystallization of the reciprocal system consists of six fields, three ternary eutectics and one transition point.

3. The system is the simplest representative of a new diagonal-belt eutectic type.

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**** See Consultants Bureau English Translation, p. 2171.

CRYOSCOPIC INVESTIGATION OF THE SYSTEM NAPHTHALENE-IODINE-MERCURIC IODIDE, I.

P. A. Smirnov

Formation of ternary systems is usually accompanied by solvation, complex-formation, association, or polymerization. These processes have attracted, and are still attracting, the attention of many investigators since they involve clarification of the properties of solutions (especially electrolytes).

In our investigation of the system naphthalene-iodine-mercuric iodide, we aimed at elucidating the effect of iodine on a solution of mercuric iodide in fused naphthalene. In our experimental conditions it was to be expected that this effect would be manifested in one of the two following directions: 1) the iodine would form complexes with HgI_2 (polyiodides); 2) the iodine would only facilitate association (or dissociation) of the mercuric iodide molecules.

The literature contains reports of the formation of polyiodides of various metals both in aqueous and nonaqueous solutions. KI with iodine in aqueous and alcoholic solutions forms the triiodide KI_3 [5]. A polyiodide of the same composition is formed when iodine and potassium iodide are dissolved in liquid SO_2 [1].

Plotnikov and others [2] investigated the electrical conductivity of iodides of the alkali metals in liquid iodine and arrived at the conclusion that the conductivity is caused by dissociation of polymers of polyiodides. Meyer [3] obtained polyiodides of the alkaline earth metals: BaI_4, SrI_4, CaI_4. Remy [4] observes (concerning polyiodides of the alkali metals): "di-, tetra-, and hexaiodides mainly of the heavy metals (Cu and Hg) also exist." Jorgensen [5] prepared mercuric hexaiodide HgI_8 in aqueous alcoholic solution. Polyiodides are only stable when a third component participates in their formation [6]. Polyiodides are not formed in solutions of mercuric iodide in liquid iodine [7].

The literature thus contains a series of statements about the formation of polyiodides of various metals, including polyiodides of mercury. In some cases iodine does not form polyiodides with a metallic iodide, notably with HgI_2.

EXPERIMENTAL

The naphthalene had m.p. 80.5°. The mercuric iodide was purified by solution in ethyl alcohol followed by removal of the solvent. Iodine was sublimed and dried in a desiccator over KOH.

The melting points were determined in a Beckmann apparatus. A first series of experiments was performed in the following sequence: 1) The melting point of a weighed sample of pure naphthalene was determined; 2) to the naphthalene was added a weighed amount of iodine, and after solution in the fused naphthalene, the solidification point of the solution was determined; 3) to the iodine solution in naphthalene was added a weighed amount of HgI_2; after this had dissolved, the melting point was again determined. The difference between the melting point (Δt_1) of pure naphthalene and the melting point of the solution of iodine in naphthalene enabled calculation of the molecular weight of the iodine.

From the difference (Δt_2) between the temperatures of solidification of the solution of iodine in naphthalene and that of the same solution after addition of HgI_2, the molecular weight of mercuric iodide was calculated according to the formula:

$$M = \frac{K \cdot a \cdot 1000}{G\Delta t},$$

where $\underline{K}$ is the cryoscopic constant of naphthalene, 6.9; $\underline{a}$ is the weight of the substance whose molecular weight was determined; Δt is the depression of the solidification point of the solution; $\underline{G}$ is the weight of the solvent.

In a second series of experiments the order of addition of iodine and HgI_2 to the naphthalene was reversed: 1) mercuric iodide was first dissolved in naphthalene and the molecular weight was determined; 2) iodine was then

TABLE 1

First Series of Experiments.

Mol. wt. of I_2 = 254; mol. wt. of HgI_2 (calc'd. from the formula) = 454; weight of naphthalene 19.74 g

No. of prep.	Weight of iodine (g)	Millimoles in 1000 g naphthalene	Amt. of I_2 added to solvent (%)	Δt	Mol. wt. of iodine found	Wt. of HgI_2 (in g)	Millimoles HgI_2 in 1000 g solution	Δt	Mol. wt. HgI_2 found
1	0.2428	47.80	1.23	0.32	265	0.1166	12.93	0.06	679
2	0.1302	25.78	0.66	0.18	253	0.1166	12.93	0.06	679
3	0.0976	19.36	0.49	0.13	262	0.1166	12.93	0.06	679
4	0.0750	16.78	0.38	0.10	262	0.1166	12.93	0.06	679
5	0.0700	13.91	0.35	0.10	245	0.1166	12.93	0.06	679
6	0.0500	9.95	0.25	0.07	250	0.1166	12.93	0.06	679
7	0.0142	2.83	0.07	0.02	248	0.1579	17.60	0.08	690

TABLE 2

Second Series of Experiments

No. of prep.	Wt. of naphthalene (in g)	Wt. of HgI_2 (in g)	Millimoles HgI_2 in 1000 g naphthalene	Δt_1	Mol. wt. HgI_2 found	Wt. of iodine (in g)	Millimoles iodine in 1000 g solution	Δt_2	Mol. wt. iodine found
1	19.75	0.0800	8.93	0.07	399	–	–	–	
2	19.74	0.1166	12.93	0.10	407	–	–	–	
3	19.99	0.1180	12.92	0.10	407	0.2458	47.82	0.34	250
4	19.74	0.1166	12.93	0.10	407	0.2000	39.49	0.27	259
5	19.74	0.1366	15.13	0.11	434	0.0764	15.18	0.10	267
6	19.74	0.1166	12.93	0.10	407	0.0651	12.98	0.09	252

introduced and its molecular weight was determined. The results of this series of experiments are set forth in Table 2, where Δt_1 denotes the difference between the solidification temperatures of pure naphthalene and of the solutions of HgI_2 therein; Δt_2 is the difference between the temperatures of solidification of HgI_2 solution in naphthalene and of the same solution with addition of iodine.

EVALUATION OF RESULTS

The results of the cryoscopic investigation of the system naphthalene-iodine-mercuric iodide set forth in Table 1 show that, regardless of the amount of iodine previously added to the naphthalene, the molecular weight of the HgI_2 remains constant (679) and differs considerably from the molecular weight calculated according to the formula (454). Such a great exaltation of the molecular weight of HgI_2 in the conditions of our experiments may be explained either by formation of polyiodides or by association of molecules of HgI_2 in naphthalene solution. The ratio between the quantities of iodine and HgI_2 in our experiments varied over fairly wide limits: in the first experiment 3.7 moles iodine were taken for 1 mole HgI_2; in experiment 8 only 0.16 mole iodine was taken per mole HgI_2, i.e., an amount clearly insufficient for the formation of even a triiodide. If polyiodides had been formed in our experiments, then the varying amounts of iodine initially added to the naphthalene should have been reflected in the magnitude of the molecular weight of the compounds of iodine and mercury formed. The non-dependence of the magnitude of our determined value of the (apparent) molecular weight of HgI_2 on the amount of initially added iodine justifies the conclusion that polyiodides are not formed in our experiments. This conclusion is also supported by the results of the experiments set forth in Table 2. The molecular weight of HgI_2 is first (without previous addition of iodine) determined. In all cases it was close to 407 (a slight deviation only occurs in experiment 5), i.e., the molecular weight of HgI_2 determined in the absence of iodine was considerably below the calculated value (454). Such a ratio between the found and calculated molecular weights is a definite criterion that mercuric iodide dissolved in fused naphthalene undergoes dissociation.

In experiments 3, 4, 5, and 6 (Table 2), iodine was added to the solution of mercuric iodide in naphthalene, after which the molecular weight of the iodine was determined. In all cases the obtained molecular weight of iodine was close to the calculated value within the limits of experimental error. This justifies the following conclusions:

1) The iodine added to the solution of HgI_2 in naphthalene does not combine with the salt, i.e. polyiodides are not formed in this case.

2) The HgI_2 moleculules do not undergo association after addition of iodine; in the event of their association, the depression would not correspond to the calculated molecular weight of iodine.

Consequently, the second series of experiments also confirms our theory that HgI_2 and mercuric iodide do not form polyiodides in fused naphthalene. In such an event, the considerable elevation (679 instead of 454) of the molecular weight of HgI_2, established in the first series of experiments, can only be explained by association of the molecules of this salt, which would occur under the influence of the iodine previously added to the naphthalene. Without previous addition of iodine (expts.1 and 2 in Table 2) no association of HgI_2 molecules is observed. Similarly, the addition of iodine after dissolution of HgI_2 in naphthalene (expts. 3-6, Table 2), does not bring about association of the molecules of this salt. The associating effect of iodine when introduced into naphthalene before dissolution of mercuric iodide in the latter and the absence of this effect when the iodine is added after dissolution of the HgI_2 may be explained in the following way. When HgI_2 is introduced into a solution of iodine in naphthalene, the molecules of this salt are first of all subjected to the action of the iodine in solution and they associate under the influence of the latter. It is possible that already associated molecules of mercuric iodide are then solvated. But when mercuric iodide is dissolved in pure naphthalene, its molecules are first of all subjected to solvation; the solvated molecules can no longer associate when iodine is added afterwards because the solvation shell formed round the HgI_2 molecules is a barrier to the action of the added iodine on them.

The degree of association of HgI_2 (according to Walden [8]) may be approximately calculated on the basis of the van't Hoff coefficient: $i = 454/679 = 0,67$; hence the degree of association $\underline{x} = 1/i = 1/0.67 = 1.495$, or 1.5. Here $\underline{x}$ indicates how many times the found (apparent) molecular weight is greater than the calculated one (coefficient of association). The 1.5 times increase of molecular weight in our conditions may have the following very simple explanation: under the influence of iodine, the molecules of HgI_2 are associated into triple molecules of $(HgI_2)_3$ with a molecular weight of 1362. The associated molecules afterwards undergo electrolytic dissociation with complete breakdown into two ions, so that Δt is increased by a factor of 2, and the molecular weight is correspondingly halved, i.e., it becomes equal to 681 (in our experiments 679)*.

Plotnikov and co-workers [7] studied the electrical conductivity of solutions of iodides of a series of metals in liquid iodine or in $AlBr_3$ and came to the conclusion that the electrical conductivity is related to the association of the molecules of the dissolved substance. The iodides are only electrically conductive when their molecules are associated, i.e., only when the molecules of iodides undergo dissociation according to the scheme:

$$(MeI)_n \rightleftharpoons Me_nI^+_{n-m} + mI^-$$

Possibly a similar dissociation occurs of the molecules of mercuric iodide in our experimental conditions.

As we have already observed, more specific conclusions about all the processes taking place in the system naphthalene—I_2—HgI_2 necessitate a closer study of this system.

SUMMARY

The cryoscopic investigation of the system naphthalene—I—HgI_2 enables the following preliminary conclusions to be reached:

1) Polyiodides are not formed when iodine and mercuric iodide are dissolved in fused naphthalene.

2) The molecules of HgI_2 undergo association under the influence of iodine which has beforehand been added to the naphthalene.

3) Iodine does not bring about association of HgI_2 in solution in naphthalene if the iodine is added last.

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CRYOSCOPIC INVESTIGATION OF THE SYSTEM

NAPHTHALENE-IODINE-MERCURIC CHLORIDE. II.

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In the investigation of nonaqueous solutions great attention is being paid —as previously noted by us [1]—to solvation and complex-formation. Sakhanov [2] explained the anomalous electrical conductivity of solutions from the standpoint of conductive complexes. Similarly Walden [3], in his numerous investigations in the field of nonaqueous solutions, explained the conductivity by polymerization and solvation of the dissolved substances. Electrical conductivity of solutions is usually explained by formation of complexes and solvates in them. An unanswered question, however, is to which of the cited processes in solutions should be attributed a high significance and to which a minor significance. This question is undoubtedly of fundamental importance for the theory of solutions. It would only be possible to establish the individual influence of each of the processes taking place in solutions on the properties of the latter if we were able to select and investigate systems in which the sole process taking place was either solvation or association or complex-formation. It is true that the two latter processes may proceed in solution side by side with solvation.

In our investigation of the system naphthalene-iodine-mercuric iodide [1] we established that association of HgI_2 molecules takes place under the influence of previously added iodine, but polyiodides are not formed. The I^- ions, of mercuric iodide, and the I_2 molecule, are mutually polarized. The increased magnitude of the dipole of HgI_2 due to the polarization facilitates association of these molecules. The Cl^- ion possesses a higher polarizing power than the I^- ion [4]; we may therefore suggest that $HgCl_2$ forms complexes with the strongly polarized I_2 molecules.

In this research we continue the elucidation of the problem of the influence of iodine on mercuric iodides with reference here to $HgCl_2$.

EXPERIMENTAL

The experimental procedure and apparatus have been described previously [1]. The reaction taking place in a solution of I and $HgCl_2$ in naphthalene proceeds slowly, and it is necessary to heat the solution at 81-85° for about 7 hours. In these circumstances, in all the experiments in this research the solution of mercuric chloride and iodine in naphthalene was kept at 81-85° for 7 hours before determination of the freezing point. The iodine color of the melt in all cases gradually became weaker during the heating period. A blank experiment in which iodine was heated in naphthalene (without $HgCl_2$) for 7 hours at 81-85° showed that in our experimental conditions the iodine substantially does not volatilize and the color of the melt remains unchanged.

In a first series of experiments the procedure was as follows: 1) Determination of solidifying point of naphthalene; 2) addition of weighed amount of mercuric chloride to weighed amount of naphthalene, determination of solidifying point and calculation of depression (Δt_1); 3) addition of weighed amount of iodine to solution of $HgCl_2$ in naphthalene, determination of solidifying point and fresh calculation of depression of solidifying point (Δt_2) (Table 1).

TABLE 1

Naphthalene Taken for Each Experiment 20 g

No. of expt.	Weight of $HgCl_2$ (in g)	Δt_1	Weight of iodine (in g)	Δt_2	Δt calculated	$\Delta t - \Delta t_2$	Amount of iodine taken (in g)	Millimoles iodine combined on basis of 1000 g naphthalene
1	0.1000	0.13	0.0220	0.02	0.03	0.01	0.007358	1.45
2	0.1000	0.13	0.0200	0.02	0.03	0.01	0.007358	1.45
3	0.1000	0.13	0.0468	0.05	0.06	0.01	0.007358	1.45
4	0.0500	0.07	0.0468	0.05	0.06	0.01	0.007358	1.45
5	0.1000	0.13	0.0514	0.04	0.07	0.03	0.0220	4.35
6	0.1000	0.13	0.0600	0.08	0.08	0	0.0600	11.81
7	0.1000	0.13	0.0900	0.09	0.12	0.08	0.05889	11.6

A second series of experiments was performed in the following order (Table 2): 1) Determination of solidifying point of naphthalene; 2) addition of weighed amount of iodine to weighed amount of naphthalene, determination of solidifying point and calculation of depression (Δt_1); 3) addition of weighed amount of mercuric chloride to solution of iodine in naphthalene, determination of solidifying point and calculation of depression Δt_2.

The last two columns of Table 1 contain the number of grams and millimoles of combined iodine; the fifth column of Table 2 contains the number of grams and millimoles of combined mercuric chloride. These values were obtained in the following manner.

TABLE 2

Naphthalene taken for all tests 20 g.

No. of expt.	Weight of iodine (in g)	Δt_1	Weight of $HgCl_2$ (in g)	Δt_2	Δt calculated	$\Delta t - \Delta t_2$	No. of grams of combined $HgCl_2$	Millimoles of $HgCl_2$ combined, on basis of 1000 g naphthalene
1	0.0440	0.06	0.1000	0.09	0.13	0.04	0.0315	5.8
2	0.0468	0.06	0.1000	0.10	0.13	0.03	0.0236	4.35
3	0.0508	0.07	0.1000	0.04	0.13	0.09	0.0710	13.07
4	0.0600	0.08	0.1000	0.05	0.13	0.08	0.0630	11.6
5	0.0882	0.12	0.1000	0.09	0.13	0.04	0.0315	5.8

That depression Δt, was calculated which would be caused by addition of a given weight of iodine (or $HgCl_2$), and from the difference $\Delta t - \Delta t_2$ was calculated the number of grams of combined iodine (or $HgCl_2$). The obtained amount of iodine (or $HgCl_2$) was recalculated on the basis of the content in 1000 g naphthalene and expressed in millimoles.

EVALUATION OF RESULTS

We see from Table 1 that: 1) With an iodine quantity of 0.0220 to 0.0468 g and a $HgCl_2$ weight of 0.1000 g, the latter combines with 1.45 millimoles of iodine (converted to 1000 g naphthalene).

2) With an iodine weight of 0.0514 g to 0.0936 g and an $HgCl_2$ weight of 0.1000 g, the amount of iodine combined is 4.35 to 11.6 millimoles; this amount is the maximum that can be bound by 0.1000 g mercuric chloride, since from 0.0600 g iodine (expt. 6) and from 0.0960 g iodine one and the same amount of it is bound.

3) In experiments 5-7 the number of millimoles of bound iodine is a multiple of 1.45; this regularity permits the conclusion that in all the above cases definite compounds of iodine with mercuric chloride are formed.

4) In experiments 3 and 4, with identical amounts of iodine (0.0468 g) and different amounts of $HgCl_2$, the number of millimoles of combined iodine is the same. Evidently 1.45 millimoles is the minimum amount of iodine that can be bound by 0.0500 g $HgCl_2$.

The following facts emerge from an evaluation of the second series of experiments (Table 2).

1) The number of millimoles of combined mercuric chloride in all the experiments is a multiple of 1.45. This regularity, like that noted for the first series of experiments, is undoubtedly also evidence that iodine and mercuric chloride form definite chemical compounds.

2) In connection with experiments 1 and 5, in each case 5.8 moles $HgCl_2$ are bound. The mystery is explained by comparing the amounts of iodine combined with these amounts of $HgCl_2$. As we saw from the first series of experiments, with iodine amounts in the range of 0.0220 to 0.0468 g the amount combined is 1.45 millimoles, while in the range of 0.0600 to 0.0936 g the amount combined is 11.6 millimoles. We can therefore conclude that in the first experiment (Table 2), out of 0.0440 g iodine, 1.45 moles is bound, while in expt. 5 out of 0.0882 g 11.6 millimoles are bound, i.e., in the case of the larger amount of iodine one and the same amount of $HgCl_2$ combined with more iodine.

3) Taking from Tables 1 and 2 those experiments in which the amounts of iodine dissolved in naphthalene are either identical or very similar and comparing them with the amounts of combined $HgCl_2$ (Table 2), we can see that iodine and $HgCl_2$ form complex compounds in fused naphthalene. These comparisons are shown in Table 3.

Comparison of the results in Tables 1 and 2 gives an indication of the composition of the complex.

TABLE 3

Weight of iodine (in g)		Weight of $HgCl_2$ (in g)		Ratio of millimoles of combined $HgCl_2$ and I_2	Formula of complex compounds
Number of experiment					
2nd series	1st series	2nd series	1st series		
1 0.0440	3 0.0468	1 0.1000	3 0.1000	5.8 : 1.45 = 4	$4HgCl_2 \cdot I_2$
2 0.0468	4 0.0468	2 0.1000	4 0.0500	4.35 : 1.45 = 3	$3HgCl_2 \cdot I_2$
2 0.0468	3 0.0468	2 0.1000	3 0.1000	4.35 : 1.45 = 3	$3HgCl_2 \cdot I_2$
3 0.0508	5 0.0514	3 0.1000	5 0.1000	13.07 : 4.35 = 3	$3HgCl_2 \cdot I_2$
4 0.0600	6 0.0600	4 0.1000	6 0.1000	11.6 : 11.8 = 1	$HgCl_2 \cdot I_2$
5 0.0882	7 0.0900	5 0.1000	8 0.1000	5.8 : 11.6 = 0.5	$HgCl_2 \cdot I_2$

On comparing the results of our investigations of the systems naphthalene—I_2—HgI_2 [1] and naphthalene—I_2—$HgCl_2$, we arrive at the conclusion that the effect of iodine on HgI_2 dissolved in fused naphthalene differs from the effect on $HgCl_2$. In the former system the only effect of the iodine is to cause association of HgI_2; in the second system complexes of iodine with molecules of $HgCl_2$ are formed.

SUMMARY

1. Cryoscopic investigation of the system naphthalene-iodine-mercuric chloride permits the conclusion that $HgCl_2$ with iodine forms complexes, polyhalides.

2. The probable formulas of these polyhalides were found to be: 1) $4\,HgCl_2 \cdot I_2$; 2) $3HgCl_2 \cdot I_2$, 3) $HgCl_2 \cdot I_2$ and 4) $HgCl_2 \cdot 2I_2$.

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SOLUBILITY IN THE SYSTEM KSCN – K_2SO_4 – H_2O

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We carried out an investigation of the equilibria in the system KSCN–K_2SO_4–H_2O at 25 and 40° for the purpose of obtaining experimental data for the joint solubility in water of two salts with a common cation and markedly differing from each other in respect to their individual solubilities and to the structures of their anions. This investigation is a continuation of research by one of us on the effect of unlike anions of differing structures on the change of individual solubilities of the salts in ternary solutions of aqueous-salt systems with a common cation [1].

The system KSCN–K_2SO_4–H_2O has not been studied completely, as far as could be judged from the literature. We studied this sytem at the above-mentioned temperatures by the well-known isothermal method. The composition of the liquid phase was determined on the basis of quantitative determinations of SCN^- and SO_4^{--}. The composition of the solid phase present in equilibrium with the solution was established by observations under the microscope of the external appearance of the crystals of the solid. The solid phases for the univariant curves of the isotherms are the individual salts, while those for the eutectic points are mixtures of salts.

It should be noted that the period necessary for attainment of the equilibrium state in the system KSCN–K_2SO_4–H_2O increased with rising concentration of KSCN in the liquid phases: at KSCN concentrations of 45% by weight and higher, the equilibrium was established after 24–30 hours.

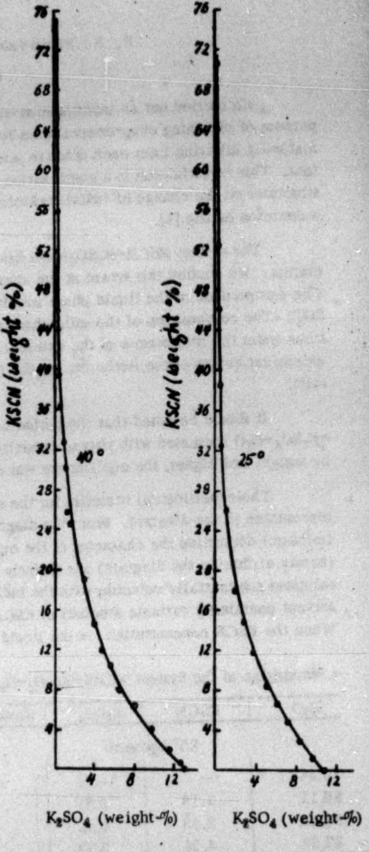
The experimental material for the system KSCN–K_2SO_4–H_2O is set forth in the table and graphically represented in the diagram. From the diagram we see that the branches of crystallization of K_2SO_4 in both of the isotherms determine the character of the equilibria in the system, whereas the branches of crystallization of KSCN (barely visible on the diagram) are entirely without significance since the solubilities of this salt in the eutonic solutions substantially coincide with the individual solutibilities. The solubility of K_2SO_4 in an aqueous-saline solvent containing variable amounts of KSCN decreases, as would be expected, with rising concentration of KSCN. When the KSCN concentration in the liquid phase reaches slightly more than 46% by weight, almost complete

Composition of the System KCNS–K_2SO_4–H_2O (in weight %)

H_2O	KSCN	K_2SO_4	Solid phase	H_2O	KSCN	K_2SO_4	Solid phase
25° isotherm				40° isotherm			
89.24	–	10.76	K_2SO_4	86.90	–	13.10	K_2SO_4
89.11	1.18	9.71		86.88	0.48	12.64	
88.55	3.03	8.42		86.03	2.10	11.87	
87.93	4.94	7.13		86.61	3.89	9.50	
87.17	6.63	6.20		85.53	6.42	8.05	
86.08	8.68	5.24		85.47	8.12	6.41	
83.98	11.80	4.22		83.79	10.54	5.67	
81.91	15.04	3.05		82.89	11.94	5.17	
79.66	18.20	2.14		81.45	14.42	4.13	
74.48	24.07	1.45		77.64	19.31	3.05	
66.90	32.50	0.60		73.85	24.46	1.69	
61.12	38.57	0.31		72.97	25.75	1.28	
53.65	46.15	0.20		68.92	30.06	1.02	
47.39	52.51	0.10		66.32	32.83	0.85	
				62.46	36.75	0.79	
29.36	70.60	0.04	K_2SO_4 + KSCN	59.93	39.63	0.44	
29.30	70.70	–	KSCN	53.48	46.30	0.22	
				43.97	55.9	0.13	
				25.73	74.24	0.03	K_2SO_4 + KSCN
				25.69	74.31	–	KSCN

salting-out of the K_2SO_4 occurs, although up to the eutonic points considerable portions of the univariant curves still remain in both isotherms. Consequently, the solutions of KSCN only possess adequate solvent power for K_2SO_4 over a specific range of concentrations, since unsaturated solutions of KSCN with salt concentrations above 46% by weight, as well as the eutectic solutions, contain (as evident from the table) extremely small amounts of K_2SO_4 which lack practical significance.

The solubility of salts in water is dependent to a certain, not yet precisely established degree on the interaction of ions of the dissolving salt with water molecules; the energetic characteristics for a given ion are determined by the value of its energy of hydration [2, 3]. In making a comparative evaluation of the experimental data for the solubility in the system $KSCN-K_2SO_4-H_2O$ we start from the premise that the solubilities of KSCN and K_2SO_4 in binary and ternary systems are fundamentally and specifically governed by the interaction of the anions with molecular water, the intensity of this interaction being determined not only by the charge but also by the structure of the ion [3]. In such an evaluation we may assume to a first approximation that the behavior of the common cation and its influence on the establishment of the equilibrium state in aqueous-saline systems in the given conditions do not depend on the anion forming a salt with the cation.



In the system which we have studied, the salts contain anions of differing structures. The triatomic anion SCN^- (with a linear configuration) contains —as follows from its electronic structure: N : : : C : $\underset{\cdot\cdot}{\overset{\cdot\cdot}{S}}$: , —C as the central atom with a coördination number of 2 [4]. The C atom is compressed from two sides by the two non-identical hemispheres of the atoms of N and S which function in the KSCN structure as packing spheres. The distance between the atoms of N and S in the SCN^- group, judging by the radii of the covalent bond, is 2.96 A, which only differs slightly from the calculated distance of 2.94 A, obtained by X-ray investigation of potassium thiocyanate crystals [4]. Coupling of N, S and C atoms gives an anion of low symmetry, fairly long length and an evidently reduced effective action of the charge. Such an anion, considering also the special features of its structure, which are generalized in the linear configuration, is incapable of any considerable development of electrostatic forces, as adequately reflected in the low value of the hydration energy of SCN^-, equal to 72 kcal/g-ion and the m.p. of KSCN of 176° (low for ionic crystals).

The tetrahedral configuration of the $SO_4^{=}$ anion, unlike the SCN^- anion, has a well-defined general symmetry and, evidently, a symmetrical arrangement of the ionic charge in the space of the anionic group which consists of elements of similar properties. The magnitude of the hydration energy of the anion, equal to 243 kcal/g-ion, points to quite intensive interaction of $SO_4^{=}$ with molecules of water, although it does not lead to formation of thermodynamically stable complexes.

The high solubility of KSCN in water, in addition to other factors, bears a definite and specific relation to the weakness of the interaction of the SCN^- ion with molecules of water in solution, the degree of which interaction is greatly influenced by the above-outlined linear configuration of the anion. The bond energy of the SCN^- anion with water molecules may to some extent be compared to the energy with which water molecules are linked to one another in the liquid state, i.e., the bonds developed between the anion and water molecules are unstable; they are often broken and formed again and lack a precise coördinative character. The SO_4^{--} anion, bearing in mind its double bond and high degree of symmetry, possesses a marked orientating action on water molecules, due to which the true value of the dielectric constant of water may be appreciably lowered. Consequently, among the factors determining the relatively low (for readily soluble salts) values of the solubility of K_2SO_4 at various temperatures, the most important is the intensive reaction of SO_4^{--} with molecules of water in solution.

It may be assumed that when ions of SO_4^{--} and SCN^- come into contact in ternary systems, the marked difference between their interactions with water molecules is maintained in full measure and that the actual influence of the common K^+ cation on the character of the interaction of each of the SO_4^{--} and SCN^- anions with molecules of water remains unchanged on transition from binary solutions to ternary solutions. As a general conclusion, we must emphasize that the markedly differing influence of the salts in the system $KSCN-K_2SO_4-H_2O$ on their joint solubility is a definite function of the difference in the behavior of the two anions toward molecules of water, and this behavior in turn is determined by the differing configurations of the anions.

SUMMARY

1. The solubility in the system $KSCN-K_2SO_4-H_2O$ was studied at 25 and 40°.

2. The necessity is noted of consideration of the structural data for the anions for characterization of the solubility in the binary and ternary aqueous-saline systems.

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* See Consultants Bureau English Translation 617.

to see another in the liquid state, i.e., the bonds developed between [illegible]

It may be assumed that [illegible]

SUMMARY

1. The solubility [illegible]

2. The [illegible]

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Received November [illegible]

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INVESTIGATION OF METASTABLE EQUILIBRIA BETWEEN LIQUID PHASES. III.

I. L. Krupatkin

In the previous communications an examination was made of the theoretical bases for study of metastable equilibria between liquid phases; two types of these were studied and two new forms of equilibrium diagrams were obtained in this connection. The study of metastable liquid-phase equilibria in three-component systems revealed their close connection with solvent systems [1]. A more detailed elucidation of this connection necessitates a study of a ternary system in which one of the components is in the solid state and dissolves in the other two which are present in the given conditions in the liquid state. It is necessary to actualize the case of solubility of a solid in a liquid mixture of two solvents which do not form stable chemical compounds between themselves. A further requirement is that each of the solvents should form with the dissolved substance a system with metastable stratification. In these conditions we should come close to clarification of the very character of systems with metastable equilibrium between the liquid phases, to clarification of the behavior of compositions of such systems as a function of the temperature. The stated conditions are fulfilled, as preliminary experiments revealed, in the three-component system sulfur-diphenylamine-β-naphthylamine. The study of this sytem is the subject of this paper.

The only binary system involving these components that is mentioned in the literature is sulfur-diphenylamine [2]. Crystallization in this system takes place according to the usual eutectic type. The eutectic point is at 92% diphenylamine and 8% sulfur, and it corresponds to a temperature of 51.5°. Below the sulfur crystallization curve is the curve of the equilibrium between the liquid phases with an upper critical temperature of solution of 104°, corresponding to a composition of 32% diphenylamine and 68% sulfur. Above the stratification curve is a small horizontal portion of the crystallization curve of sulfur. The remaining two systems in the given ternary system —sulfur-β-naphthylamine and diphenylamine-β-naphthylamine —are investigated in this research. The system sulfur-β-naphthylamine is similar to the binary system sulfur-diphenylamine; in it is likewise established a metastable equilibrium between the liquid phases. In the two-component system diphenylamine-β-naphthylamine no compound formation between the components is reflected on the curve of crystallization. In the liquid phase of this sytem, however, the existence of unstable compounds is possible since diphenylamine tended to form similar compounds, e.g., with quinoline.

Hence, in the three-component system sulfur-diphenylamine-β-naphthylamine we have solubility of the sulfur in a mixture of the two liquid amines (diphenylamine and β-naphthylamine) and dissociation of the associated sulfur in them. Both of the amines in the systems with sulfur form a metastable equilibrium between the liquid phases. Unstable complexes are possibly formed between the two amines. Thus, the given ternary system fully satisfies the above-indicated conditions.

EXPERIMENTAL AND EVALUATION OF RESULTS

The following reactants were taken for the investigation: sulfur recrystallized from benzene with m.p. 117°, and apparently consisting of a mixture of the monoclinic and rhombic forms [3]; diphenylamine, chemically pure, with m.p. 54°; β-naphthylamine "pure" with m.p. 112°.

The sulfur and diphenylamine were checked against the system sulfur-diphenylamine as detailed in the literature. The check showed agreement with the literature data. The research was carried out by Alekseev's method [4] in sealed ampoules in an oil thermostat.

System sulfur-β-naphthylamine was studied by fusion and stratifiability. The results are set forth in Table 1 and plotted in Figure 1. The fusion curve of this system has the usual eutectic form; the eutectic point is not low, has a composition of 35% β-naphthylamine and corresponds to a temperature of 100°. The sulfur crystallization curve has, above the curve of metastable stratification, a horizontal portion at 103° extending over the concentration range of 60 and 80% sulfur. Below the sulfur crystallization curve is the curve of metastable stratification with an upper critical solution temperature at 100.5°, displaced toward the sulfur corner, coinciding with the composition 75.05% sulfur and 24.95% β-naphthylamine.

Binary system diphenylamine-β-naphthylamine was studied by the fusion method. The results are set forth

TABLE 1

Equilibrium in the System Sulfur-β-Naphthylamine

No. of expt.	Sulfur (wt. %)	β-Naphthylamine (wt. %)	Temperature	
			of crystallization	of stratification
1	0.00	100.00	112.0	–
2	13.00	87.00	107.0	–
3	20.56	79.44	104.5	–
4	30.00	70.00	102.0	–
5	35.00E*	65.00	100.0	–
6	40.35	59.65	101.0	–
7	48.50	51.50	–	96.5
8	49.86	50.14	101.5	–
9	60.00	40.00	102.5	99.0
10	65.00	35.00	–	99.5
11	70.50	29.50	103.0	100.0
12	75.05	24.95	–	100.5
13	80.30	19.70	103.0	100.0
14	100.00	0.00	117.0	–

* = eutectic point

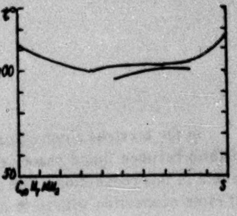

Fig. 1

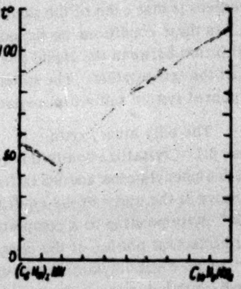

Fig. 2

in Table 2 and plotted in Figure 2. The fusion curve of this system intersects the eutectic point at 42°, the composition then being 83% diphenylamine and 17% β-naphthylamine. Formation of chemical compounds between the components was not observed. Nevertheless, as indicated previously, unstable compounds are possible in this system in the liquid phase.

TABLE 2 Equilibrium in the System Diphenylamine – β-Naphthylamine

No. of expt.	Diphenylamine (wt. %)	β-Naphthylamine (wt. %)	Crystallization temperature
1	0.00	100.00	112.0
2	9.64	90.36	105.0
3	19.14	80.86	100.0
4	29.95	70.05	94.5
5	40.00	60.00	88.0
6	49.92	50.08	81.0
7	59.90	40.10	71.0
8	69.99	30.01	60.5
9	75.00	25.00	54.5
10	80.00	20.00	46.5
11	83.00E*	17.00	42.0
12	85.06	14.94	44.0
13	90.11	9.89	47.0
14	95.00	5.00	50.0
15	100.00	0.00	54.0

*Eutectic point

The ternary system sulfur-diphenylamine-β-naphthylamine was studied by drawing polythermic sections through its prism, extending from the sulfur edge to the boundary of the binary system diphenylamine-β-naphthylamine. Six such sections were studied in all, with contents of 10, 20, 40, 60, 70 and 80% β-naphthylamine. Crystallization and stratification were studied in the polythermic sections. The data for the sections are set forth in Table 3 and plotted in Figure 3, a, b, c, d, e and f. In all the polythermic sections sulfur crystallizes with a very strong undercooling tendency, which is characteristic of systems with metastable equilibrium between the liquid phases, especially above the stratification curve. Due to this, some mixtures cannot be made to crystallize. These mixtures are indicated in the table. Each section consists of the crystallization curve of sulfur in the respective mixture of amines and the curve of metastable equilibrium between the liquid phases with the upper critical solution temperature, displaced to the sulfur corner. The metastability of the stratification in all the sections is an indication of the metastability of the whole equilibrium volume between the phases of the ternary system sulfur-diphenylamine-β-naphthylamine, i.e., of its existence entirely below the surface of crystallization of sulfur.

If the curve of the critical points is drawn through the critical points of the stratification curves of the binary systems and the sections, and if the same is done for the points of the fusion curve located above the critical points, then the projection of both curves on to the plane extending through the critical points of the binary systems will have the shape represented in Fig. 4. On this, the upper curve relates to crystallization and the lower one to metastable

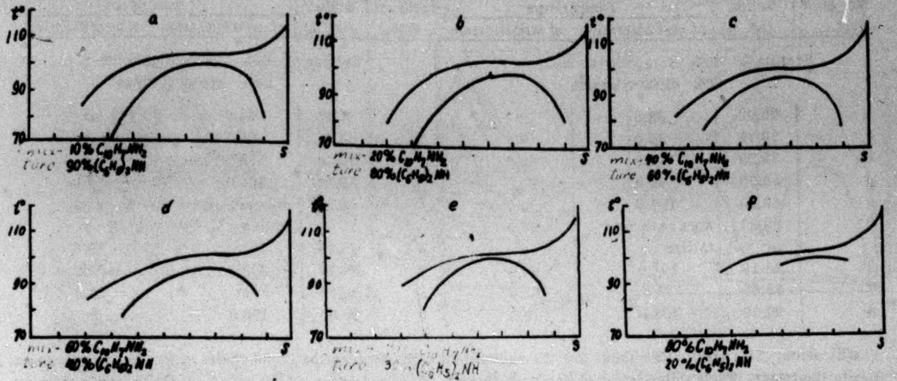

Fig. 3.

TABLE 3

Polytherms of the System Sulfur-Diphenylamine-β-Naphthylamine

No. of expt.	Sulfur (wt. %)	Temperature of crystallization	Temperature of stratification
Section No. 1: 10% β-naphthylamine, 90% diphenylamine			
1	19.88	84.0	–
2	29.82	94.0	70.0
3	39.99	99.5	86.0
4	50.00	103.0	94.5
5	60.11	103.5	99.0
6	70.00	104.0	100.0
7	80.06	105.0	99.0
8	84.91	–	94.0
9	89.89	107.0	80.0
Section No. 2: 20% β-naphthylamine, 80% diphenylamine			
1	20.00	79.0	–
2	29.84	92.0	–
3	31.07	–	81.0
4	39.97	99.0	85.0
5	50.00	101.5	93.0
6	60.60	103.0	–
7	61.99	–	97.0
8	69.39	103.0	99.0
9	80.00	104.0	96.5
10	85.65	105.0	92.0
11	86.99	–	89.0
12	87.99	106.0	87.0
13	90.00	–	81.0
Section No. 4: 60% β-naphthylamine, 40% diphenylamine			
1	19.92	84.0	–
2	30.00	89.0	–
3	34.90	–	79.0
4	40.11	94.0	85.0
5	50.00	98.0	91.0
6	60.07	101.0	95.5
7	69.95	does not crystallize	96.5
8	80.00	102.0	95.0
9	86.68	103.0	88.0
Section No. 5: 70% β-naphthylamine, 30% diphenylamine			
1	30.10	89.0	–
2	40.00	95.0	83.0
3	50.00	99.0	95.0
4	60.05	does not crystallize	99.0
5	69.90	102.0	99.0
6	79.97	103.0	97.0
7	85.03	–	92.0
8	87.00	104.0	88.0

TABLE 3 -- (continued)

No. of expt.	Sulfur (wt. %)	Temperature		No. of expt.	Sulfur (wt. %)	Temperature	
		of crystallization	of stratification			of crystallization	of stratification
	Section 3: 40% β-naphthylamine, 60% diphenylamine				Section 6: 80% β-naphthylamine, 20% diphenylamine		
1	25.00	82.5	–	1	35.96	94.0	–
2	30.12	86.0	–	2	40.00	96.0	–
3	39.89	94.0	82.0	3	50.00	100.0	–
4	50.00	98.0	91.0	4	59.10	101.0	97.0
5	60.00	100.5	95.5	5	65.12	does not crystallize	98.0
6	69.87	does not crystallize	96.0	6	75.00	ditto	99.0
7	80.19	101.0	94.0	7	80.13	103.0	99.0
8	85.65	–	91.0	8	85.65	–	98.0
9	90.00	105.0	79.0	9	90.00	106.0	–

stratification. This graph alone shows that the equilibrium space between the liquid phases of the ternary system has a saddle-like point. The saddle-like point has a temperature of 96° and occurs on the section of the ternary system containing 46% β-naphthylamine and 54 % diphenylamine in the two-component system – β-naphthylamine-diphenylamine. This composition corresponds to a 1:1 ratio between the molecules of the two amines (strictly it should be 45.83% β-naphthylamine and 54.17% diphenylamine). The projection of the crystallization curve likewise has a minimum which falls on the same section of the ternary system at a temperature of 101°. Both curves exhibit the general course of crystallization and stratification.

Starting from the polytherms of metastable equilibrium between the liquid phases, the stratification isotherms represented in Fig. 5 were plotted. A total of 4 isothermal sections was plotted through the prism of the ternary system at temperatures of 90°, 95°, 97° and 100°. The 97° and 100° isotherms are above the saddle-like point and therefore they possess two separate regions of stratification. The latter start from solubility breaks at the corresponding temperatures in the two-component systems with metastable equilibrium between the liquid phases present inside the prism and they later merge. At 96°, i.e., the temperature of the saddle-like point, they must come into contact with each other. The 90° and 95° isotherms are below the saddle-like point. Hence, in these isothermal sections both regions of stratification, starting from the solubility break in the binary systems, run together inside the prism of the ternary system into one region of stratification of the ternary system. The isotherms of metastable stratification located below the saddle-like point possess maxima of reciprocal solubility of sulfur and mixtures of the amines in the liquid state. These maxima coincide with the polythermal section which, in the binary system, diphenylamine-β-naphthylamine corresponds to the 1:1 molar ratio.

Starting from the crystallization polytherms, plots were constructed of the isotherms of crystallization of sulfur in the ternary system. A total of 5 such isothermal sections was drawn through the prism of the ternary system at temperatures of 85°, 90°, 95°, 100° and 105°. The isotherms are shown in Fig. 6. They all have a similar form with a maximum of solubility of sulfur in the mixture of amines. These maxima fall on the very same polythermal section as the maxima of mutual solubility of the components in the liquid state, namely on the section corresponding in the binary system of the two amines to 1:1 molar ratios.

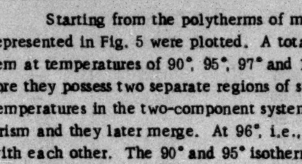

Fig. 4.

The foregoing graphical data permit the representation of the three-component system sulfur-diphenylamine-β-naphthylamine in the form of a prism. This is illustrated in Fig. 7, where B, C, and D respectively denote β-naphthylamine, sulfur and diphenylamine. The diagram clearly shows the space of the two-phase liquid state 1, 2, 3, 4, K_1, K_2, metastable at all temperatures and concentrations, with a saddle. The surface of crystallization of sulfur 5, 6, 7 is observed with its solubility maximum in mixtures of the two amines – diphenylamine and β-naphthylamine.

Consequently, the two-component system β-naphthylamine-diphenylamine is a typical solvent system in relation to sulfur, both

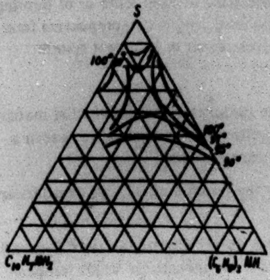

Fig. 5

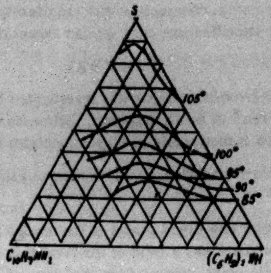

Fig. 6

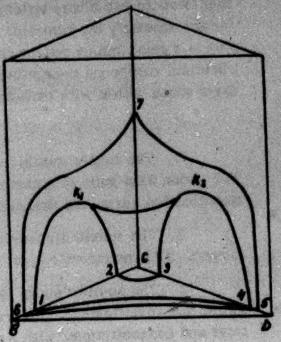

Fig. 7

in its liquid and solid state. Indeed at 95°, for example, the solubility of liquid sulfur in the separate amines is of the order of 45%, whereas in the 1: 1 molar mixture of the amines — in which the solubility of sulfur reaches a maximum — the solubility approaches 60%. At the same temperature the solubility of solid sulfur in the amines is only of the order of 30%, but in the 1: 1 mixture it reaches 45%. On the basis of the theory of solubility developed by R. V. Mertslin [1], these facts may find an explanation in the following way. First, in the binary system β-naphthylamine-diphenylamine, a chemical compound is formed with 1: 1 molar composition. Second, this compound is unstable and easily breaks down at higher temperatures even in such a nonpolar solvent as sulfur. This evidently accounts for the absence of a maximum on the fusion curve of the two-component system diphenylamine-β-naphthylamine. Third, sulfur in the associated state is not passive toward the specified compound and dissociates therein. In this latter connection, we may recall that the dissociation of associated sulfur in amines is a well-known phenomenon.

All the above-stated facts become fully understandable on the assumption of formation of a solvent system. However, an additional factor is necessary for development of solvent systems. This is a type of monotectic crystallization in the three-component system such that crystallization of one and the same component should take place throughout the whole region from one stratifying binary system (in the ternary system in question) to the other. Monotectic crystallization takes place when there is stable stratification in a system, when the curves or surfaces of stratification intersect the curves or surfaces of crystallization and one of the phases of the system disappears with change of temperature. In the case of the three-component system sulfur-diphenylamine-β-naphthylamine, throughout the whole region between the two binary systems with metastable stratification we find crystallization of one and the same component, namely sulfur; here, however, the crystallization is not monotectic since the whole surface of stratification is metastable and does not intersect the surface of crystallization. Nevertheless, as shown by the isotherms of crystallization, the solvent character of the system is also realized at temperatures above the critical temperatures of the metastable equilibrium between the liquid phases. This fact suggests that in a series of cases the two-component systems with metastable stratification may behave like systems with stable equilibrium between the liquid phases. We may, therefore, conclude that in the given systems with metastable stratification at temperatures very much higher than the temperatures of stratification, we obtain a state close to the state of latent stratification. It is clear that compositions in the latently stratified state may often behave like compositions with normal stratification.

The above discussion permits us to explain the process of development of metastable stratification. It must proceed from true homogeneity to latent stratification and from the latter to metastable stratification. The possibility of development of stable stratification by this route is not excluded.

On the basis of the above experimental material we may approach certain problems of prognosis of solvent systems. Clarification of the conditions of formation of solvent systems is particularly important due to its potential practical value in the selection of solvent systems for certain substances for which single solvents cannot be readily found. These problems were analyzed by R. V. Mertslin [1] for ternary systems involving binary systems with stable equilibrium between the liquid phases. As was shown above, when metastable stratification arises in two binary systems entering into the given ternary system and when there is compliance with the other factors necessary for formation of a solvent system, then such a system is actually developed. From this it follows that if a given binary system contains associated components capable of dissociating in each other or of forming a chemical compound susceptible to mutual dissociation with the dissolved substance, and if its components form binary systems with it with metastable stratification, then we can expect the development of a solvent system.

SUMMARY

1. The binary system sulfur-β-naphthylamine was investigated by the fusibility and stratification methods. The fusion data point to a eutectic form of fusion diagrams. Below the crystallization curve of sulfur is seen a stratification curve; the stratification is metastable at all temperatures and concentrations.

2. The system diphenylamine-β-naphthylamine was investigated by the fusion method. Its equilibrium diagram is of the eutectic type.

3. The equilibrium of the solid and liquid phases in the ternary system sulfur—diphenylamine—β-naphthylamine was investigated. The system contained a field of the two-phase liquid state, metastable at all temperatures and concentrations, with a saddle point, starting from the plane of metastable stratification of its binary systems sulfur-diphenylamine and sulfur-β-naphthylamine.

4. Suggestions are made about the possible mode of development, from the homogeneous solution, of metastable stratification and about its behavior at higher temperatures.

5. Some supplementary conditions for the practical choice of solvent systems are indicated.

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INVESTIGATION OF THE INTERACTION BETWEEN QUINOLINE AND NITROPHENOLS BY THE METHODS OF PHYSICO-CHEMICAL ANALYSIS

A. D. Kirillova and D. E. Dionisyev

Quinoline resembles pyridine [1, 2] in being a good complex-former due to the presence of a tertiary nitrogen atom which serves as an electron donor. Investigation of the interaction of quinoline with phenol by the fusion and viscosity methods [3] revealed the existence of highly dissociated compounds with the composition: $C_9H_7N \cdot 2C_6H_5OH$ and $3C_9H_7N \cdot 2C_6H_5OH$.

We set ourselves the problem of establishing the nature of the influence on the character of the interaction of the introduction of nitro groups into various positions of the phenol molecule; also the effect of the number of such groups. With this objective we studied the interaction of quinoline with o- and p-nitrophenols and with 2,4-dinitrophenol by the methods of fusion, viscosity, density and electrical conductivity.

For the investigation we used chemically pure quinoline which, after prolonged standing over KOH and two fractional distillations, had b.p. 238°, d_4^{45} 1.077, η^{45} 1.890.

o-Nitrophenol, recrystallized three times from alcohol, m.p. 44.5°, d_4^{45} 1.286, η^{45} 2.030.

p-Nitrophenol, recrystallized three times from water, had m.p. 113°, d_4^{115} 1.280, η^{115} 2.900.

2,4-Dinitrophenol twice recrystallized from alcohol, had m.p. 113.3°, d_4^{115} 1.440, η^{115} 2.990.

The system quinoline–o-nitrophenol was investigated by Bramley [3] by the colorimetric method and by the fusion method at temperatures of 30, 40, 60, and 80°. The maxima on the viscosity curves occur at approximately 58.2 wt.-% o-nitrophenol. On the basis of investigation by these methods, Bramley [3] comes to the conclusion that a molecular compound with the composition $C_9H_7N \cdot o\text{-}C_6H_4NO_2OH$ is formed. We performed an investigation of the fusion and electrical conductivity and repeated the investigation of the density and viscosity. We failed to detect the formation of a chemical compound of definite composition by the fusion method, since in the 55 to 85 mole-% range of quinoline, non-crystallizable, vitreous masses were formed (Fig. 1). The density isotherms (Fig. 2) at 45 and 55° are very slightly concave to the axis of composition of the curves. The isotherms of viscosity η at the same temperatures are curves with small, diffused maxima. The curve of the absolute temperature coefficient of viscosity a has a maximum corresponding to the composition of 50 mole% quinoline. The electrical conductivity κ was plotted at 25, 45, and 55° (Fig. 3). The electrical conductivity of the mixture rises considerably in comparison with the pure components, reaching a maximum of about 40 mole% quinoline. Correction of the electrical conductivity for viscosity $\eta\kappa$ hardly changes the position of the maxima. We also incline to the view that in this system a strongly dissociated chemical compound of the composition $C_9H_7N \cdot o\text{-}C_6H_4NO_2OH$ is formed and that the maxima of the curves of electrical conductivity and corrected conductivity $\eta\kappa$ are shifted in the direction of o-nitrophenol from the ordinates of the compound. By comparison with the system quinoline–phenol the present system has a lower viscosity, but the electrical conductivity and the corrected conductivity are considerably higher.

The system quinoline–p-nitrophenol has not previously been investigated. The fusion curve (Fig. 4) has a maximum corresponding to 50 mole-% quinoline with m.p. 89.5°, which indicates formation of a solid-phase compound of the composition $C_9H_7N \cdot p\text{-}C_6H_4NO_2OH$.

The density isotherms (Fig. 5) are concave to the axis of composition of the curves without any maxima. The viscosity isotherms are concave to the axis of composition in the p-nitrophenol region, pass through a maximum and are convex to the axis of composition in the quinoline region. The maxima flatten out with rising temperature. The curves of the absolute temperature coefficient of viscosity are similar to the viscosity isotherms. The viscosity curves suggest a chemical reaction in the system but the maxima are not correlated with the composition of a chemical compound. The isotherms of electrical conductivity (Fig. 6) rise steeply from p-nitrophenol, forming maxima at about 10-mole-% quinoline at which point they become convex to the axis of composition. Usanovich [4] regards such curves as evidence of acid-base interaction, but the position of the maximum makes it difficult to draw any conclusion about the composition of the chemical compound. Possibly in the liquid phase another, strongly dissociated, compound is formed which is incapable of crystallization; composition: $C_9H_7N \cdot 2p{-}C_6H_4NO_2OH$.

This compound is reflected on the isotherms of viscosity, electrical conductivity and corrected electrical conductivity in the form of maxima shifted in the direction of p-nitrophenol. We see that in this system the viscosity, electrical conductivity and corrected electrical conductivity are considerably higher than in the preceding systems.

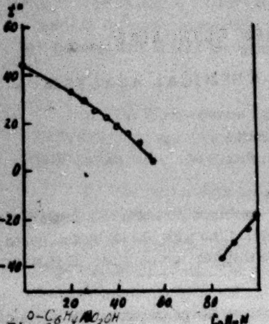


Fig. 1

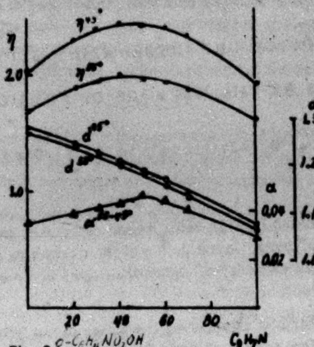


Fig. 2.

The system quinoline–2,4-dinitrophenol was also investigated by us for the first time. The melting point curve (Fig. 7) forms a maximum corresponding to 50 mole-% quinoline, which testifies to the formation of the compound $C_9H_7N \cdot 2,4{-}C_6H_3(NO_2)_2OH$.

The density isotherms (Fig. 8) are curves which are concave to the axis of composition, indicating contraction in the system. The viscosity isotherms have the same form as in the preceding system. The viscosity maximum at 95° corresponds to approximately 40 mole-% 2,4-dinitrophenol and with rising temperature it is shifted in the direction of the more viscous component (dinitrophenol). The curves of the absolute temperature coefficient of viscosity repeat the course of the viscosity curves and the maxima are formed at the same compositions. The maxima of the electrical conductivity isotherms (Fig. 9) are at 125° and 50 mole-% quinoline. With rising temperature the maxima are shiften in the quinoline direction. This displacement is accounted for by the increasing viscosity of the mixtures with falling temperature, due to which the maxima of electrical conductivity are shifted in the direction of compositions with a lower viscosity. The correction of the electrical conductivity for viscosity did not change the course of the curves which were only slightly shifted in the direction of 2,4-dinitrophenol. The curves of viscosity and electrical conductivity reflect the existence of the compound which was detected by the fusion method. The values of viscosity, electrical conductivity and corrected electrical conductivity exceed those of the preceding systems.

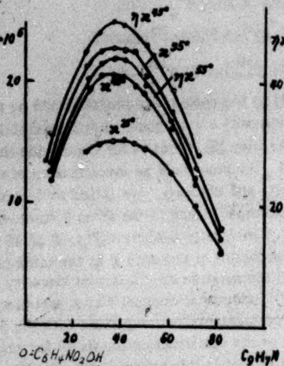
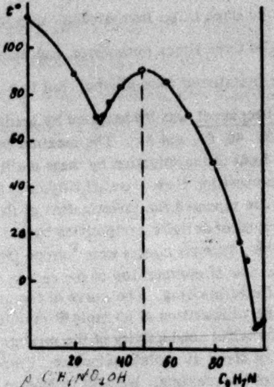


Fig. 3.



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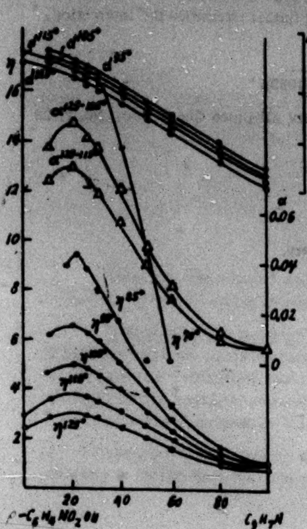

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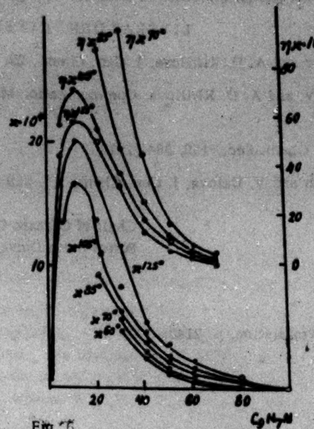

Fig. 6.

SUMMARY

1. The isotherms of viscosity, density, electrical conductivity and corrected electrical conductivity of the systhem quinoline—o-nitrophenol point to formation of an equimolecular compound in the liquid phase.

2. The fusion method demonstrated the formation in the system quinoline—p-nitrophenol of an equimolecular compound. The isotherms of viscosity, density, electrical conductivity and corrected electrical conductivity point to the occurrence of chemical interaction in the system, but the maxima of the curves are not correlated with the composition of a compound.

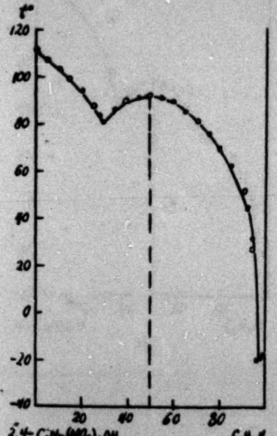

Fig. 7.

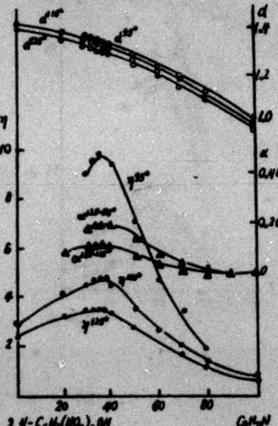

Fig. 8.

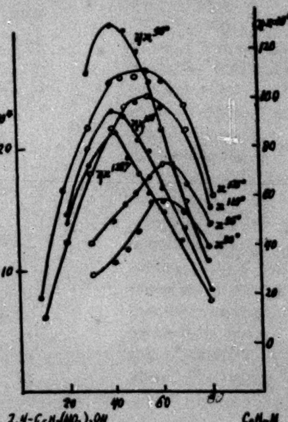

Fig. 9.

3. In the system quinoline—2,4-dinitrophenol the fusion method established the existence of an equimolecular compound. On the isotherms of viscosity, electrical conductivity and corrected electrical conductivity is reflected the existence of the compound detected by the fusion method.

4. The p-position of the nitro group in phenol intensifies the interaction with quinoline in comparison with the o-position due to the formation in o-nitrophenol of an internal hydrogen bond which hinders interaction (the ortho effect). Introduction into the phenol molecule of a second nitro group still further intensifies the interaction.

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* See Consultants Bureau Translation, p. 2143.

INVESTIGATION OF THE INTERACTION OF QUINOLINE WITH α- AND β-NAPHTHOLS BY THE METHODS OF PHYSICO-CHEMICAL ANALYSIS

A. D. Kirillova and D. E. Dionisyev

Using the methods of fusion, viscosity, density and electrical conductivity, we have studied the systems quinoline-α-naphthol and quinoline-β-naphthol which have not previously been investigated.

System quinoline-α-naphthol. The fusion curve (Fig. 1) forms one maximum corresponding to 50 mole-% quinoline and one transition point corresponding to 72 mole-% quinoline with a transition temperature of 29°, which indicates formation of two compounds: one melting congruently, corresponding to the composition $C_9H_7N \cdot \alpha\text{-}C_{10}H_7OH$ and having an m.p. of 53.5°; the second melting incongruently and with a composition difficult to determine accurately; possibly it is the compound $2C_9H_7N \cdot \alpha\text{-}C_{10}H_7OH$ or $3C_9H_7N \cdot 2\alpha\text{-}C_{10}H_7OH$.

The curves of the density isotherms (Fig. 2) are concave to the axis of composition. The curves of the viscosity isotherms have maxima which flatten out with rising temperature. We attempted to plot the viscosity isotherm at a temperature below the melting point of the compound. At 50° the viscosity maximum corresponds to approximately 45 mole-% quinoline; with rising temperature it is appreciably shifted in the direction of α-naphthol. Such a large shift of the viscosity maximum from the ordinates of the compound, even at a temperature below the melting point of the compound, indicates that the compound breaks down when still in the solid phase. The curves of the absolute temperature coefficient of viscosity α have the same forms as the viscosity isotherms.

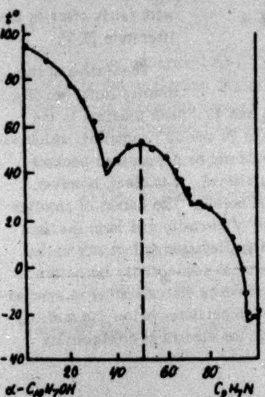

Fig. 1

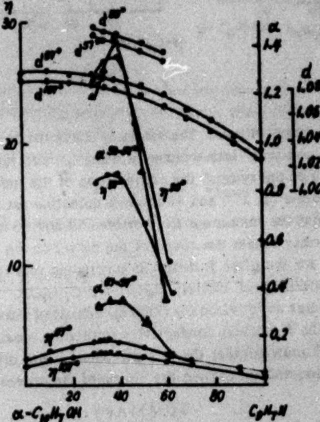

Fig. 2.

The isotherm of electrical conductivity κ (Fig. 3) at 107° has a maximum corresponding to 35 mole-% quinoline. With falling temperature an inflexion starts to form (at 97°), leading to a minimum (at 77°) which becomes more pronounced with falling temperature (57°). As we know, systems in which conductive mixtures are developed from two nonconductive substances belong to the 7th type in M. A. Klochko's classification [1]. When the correction for viscosity (ηκ) is made, the maximum of electrical conductivity may pass into a minimum with falling temperatures (due to the greatly increased viscosity). The given system vividly illustrates the gradual transition of the maximum of electrical conductivity into a minimum due to the rise in viscosity. The position of the minimum of electrical conductivity indicates the formation in the system of the compound $C_9H_7N \cdot \alpha\text{-}C_{10}H_7OH$. The correction of the electrical conductivity for viscosity shifts the maximum of electrical conductivity in the direction of quinoline. Thus, at 57° the maximum corresponds to 40 mole-% quinoline, but with rising temperature it moves in the direction of α-naphthol. From a study of the liquid phase we may conclude that the diagrams of state reflect a more stable equimolecular compound. No sign of a second compound is found.

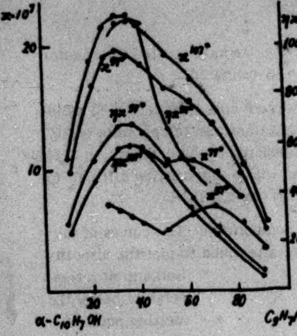

Fig. 3.

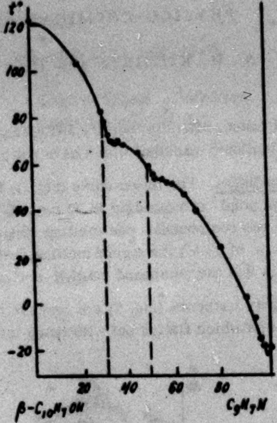

Fig. 4.

System quinoline-β-naphthol. The fusion curve (Fig. 4) has two transition points, corresponding to 34 mole-% quinoline with m.p. 71.5° and to 51 mole-% quinoline with m.p. 55°. The transition points nearly coincide with the ordinates of the compounds $C_9H_7 \cdot 2\beta\text{-}C_{10}H_7OH$ and $C_9H_7N \cdot \beta\text{-}C_{10}H_7OH$. Cases of coincidence of transition points with the ordinates of composition of compounds are met with fairly often in the literature [2,3].

The curves of the density isotherms (Fig.5) are also concave to the axis of compositions. The viscosity isotherms at 105, 115 and 125° have maxima in the region of 30 mole-% quinoline and they flatten out with rising temperature. On the 70 and 50° isotherms, which we plotted in the undercooled state of the system, the composition of the maxima could not be determined because mixtures up to 35 mole-% quinoline (at 75°) and 40 mole-% quinoline (at 50°) crystallized. It is clear, however, from the course of the curves that the maximum lies between 30 and 35 mole-% quinoline. The curves of absolute temperature coefficient of viscosity repeat the course of the curves of the isotherms of viscosity and form maxima at the same compositions. We are therefore justified in concluding that the viscosity diagrams reflect one of the compounds detected by the fusion method, namely $C_9H_7N \cdot 2\,\beta\text{-}C_{10}H_7OH$. The electrical conductivity isotherms, measured at the same temperatures as for viscosity (Fig. 6), consist of curves with maxima corresponding to approximately 25 mole-% quinoline. The electrical conductivity isotherms, measured for temperatures below the melting points of the compound (50, 70°) indicate that the 1:1 compound is not reflected on the electrical conductivity diagram. The viscosity correction did not change the course of the curves.

SUMMARY

1. Two compounds are detected in the system quinoline – α-naphthol by the fusion method: the first melting congruently, $C_9H_7N \cdot \alpha\text{-}C_{10}H_7OH$ and $2C_9H_7N \cdot \alpha\text{-}C_{10}H_7OH$ or $3C_9H_7N \cdot 2\alpha\text{-}C_{10}H_7OH$. The isotherms of viscosity, electrical conductivity and corrected electrical conductivity of the system quinoline – α-naphthol point to the existence in the liquid phase of a compound of the composition $C_9H_7N \cdot \alpha\text{-}C_{10}H_7OH$. No reflection of the second compound appears on the isotherms in question.

2. In the system quinoline – β-naphthol, by the fusion method, was detected the formation of two incongruently melting compounds, $C_9H_7N \cdot \beta\text{-}C_{10}H_7OH$ and $C_9H_7N \cdot 2\beta\text{-}C_{10}H_7OH$. Only one compound, with the composition $C_9H_7N \cdot 2\beta\text{-}C_{10}H_7OH$, is reflected on the diagrams of viscosity, electrical conductivity and corrected electrical conductivity.

3. The density isotherms of both systems consist of curves which are concave to the axis of compositions, indicating that contraction had occurred in the system.

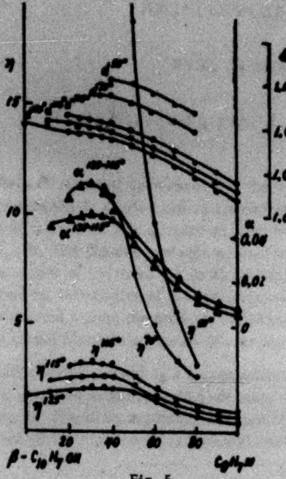

Fig. 5.

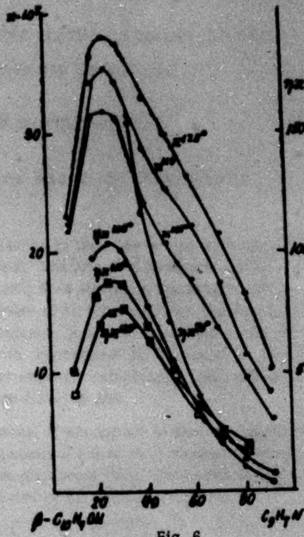

Fig. 6.

4. Introduction into the phenol molecule of an additional benzene ring weakens the interaction with quinoline. Evidently the weakening of the complex-forming properties is caused, apart from the high dissociation constant of naphthol, by steric hindrance. The β-position in naphthol is more favorable to complex formation than the α-position (the viscosity, electrical conductivity and corrected electrical conductivity are higher in the case of β-naphthol).

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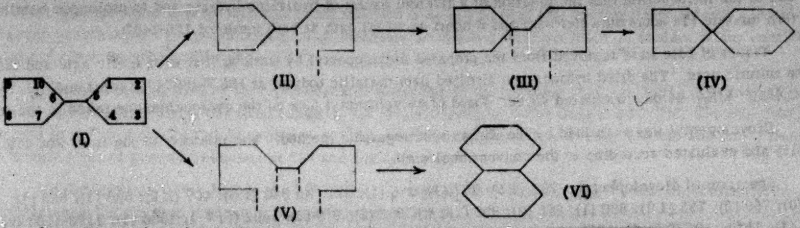
ISOMERIZATION OF POLYMETHYLENE HYDROCARBONS UNDER THE INFLUENCE OF ALUMINUM CHLORIDE

XVIII. ISOMERIZATION OF DICYCLOPENTYL

M. B. Turova-Polyak, I. E. Sosnina and E. G. Treshchova

The isomerization of hydrocarbons of the cyclopentane series by their interaction with aluminum chloride has been very completely studied and elucidated in the literature. The action of aluminum chloride on bicyclic hydrocarbons of this series, in particular on dicyclopentyl, has only been studied in cracking conditions [1]. N.D. Zelinsky and I. N. Tits [2] observed enlargement of the ring system of dicyclopentyl into the decahydronaphthalene system by the action of hydrogen iodide on cyclopentylcyclopentanol. A similar phenomenon was observed in the present research on dehydration of cyclopentylcyclopentanol with concentrated phosphoric acid. Decahydronaphthalene was detected among the products of hydrogenation of cyclopentylcyclopentene. The aim of this investigation was the study of the isomerizing action of aluminum chloride on dicyclopentyl.

Regarding dicyclopentyl as a monosubstituted cyclopentane, it was natural to assume that the products of its isomerization would be either spiro-(4,5)-decane, due to enlargement of one of the five-membered rings, or decahydronaphthalene, due to simultaneous enlargement of both five-membered rings. Formation of spiro-(4,5)-decane and decahydronaphthalene from dicyclopentyl could be represented by the following scheme:



According to this scheme, formation of spiro-(4,5)-decane may be explained in the following manner: The bond between carbon atoms 4 and 5 (II) is first ruptured. Then the hydrogen atom of carbon atom 6 migrates to carbon atoms 5 (III) and, finally, a new bond is formed between carbon atoms 6 and 4 (IV). According to the above scheme, decahydronaphthalene may be formed by simultaneous rupture of the bonds between carbon atoms 4,5 and 6,7 (V) and formation of fresh bonds between carbon atoms 4,6 and 5,7 (VI).

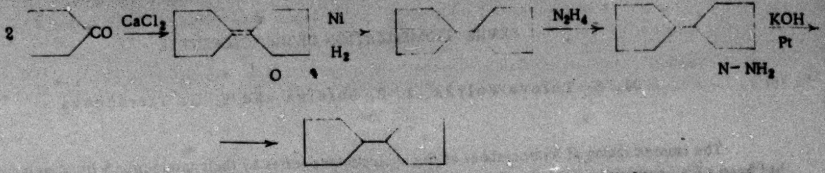
Our investigation revealed that the interaction of dicyclopentyl with aluminum chloride proceeds with considerable evolution of heat. In the couse of 1½ minutes the temperature rises from room temperature to 100-103°, after which it gradually falls. The sole product of isomerization of dicyclopentyl is decahydronaphthalene, predominantly in the trans-form. The presence of decahydronaphthalene was demonstrated by formation of naphthalene on dehydrogenation of the isomerization products and was confirmed by the Raman spectrum. The predominance of trans-decahydronaphthalene among the products of isomerization is in good accord with earlier data of N.D. Zelinsky and M. B. Turova-Polyak [3] who showed that interaction of cis-decahydronaphthalene with aluminum chloride at room temperature gives mainly trans-decahydronaphthalene. It is interesting to note that the hydrocarbon fractions obtained on isomerization of cis-decahydronaphthalene had constants [3] similar to those of the hydrocarbon fractions obtained on isomerization of dicyclopentyl.

Spiro-(4,5)-decane, whose formation should result from enlargement of one five-membered ring, was not detected among the reaction products. It has thus been established that the bicyclic system of dicyclopentyl, under the influence of aluminum chloride, just as readily undergoes isomerization with enlargement of the five-membered rings as do monocyclic hydrocarbons of the cyclopentane series.

This very type of isomerization possibly occurs in the conditions of petroleum deposits, and would then account for the absence from petroleums of such hydrocarbons as dicyclopentyl and for the presence of decahydronaphthalene.

EXPERIMENTAL

The synthesis of dicyclopentyl was accomplished according to the following scheme:



2-Cyclopentylidene-cyclopentanone was prepared by boiling cyclopentanone in a Soxhlet apparatus in presence of calcium carbide for 4 hours [1]. The ketone distilled at 128-130° (21 mm) and had n_D^{20} 1.5196; d_4^{20} 1.0221 (yield 54%).

2-Cyclopentyl-cyclopentanone was prepared in 86% yield by hydrogenation of 2-cyclopentylidene-cyclopentanone at room temperature in presence of skeletal nickel and at a hydrogen pressure of 90-107 atm. Its constants were: b.p. 107-109° (13 mm); n_D^{20} 1.4772; d_4^{20} 0.9775. MR_D 43.94; calculated 43.99. The semicarbazone of cyclopentylcyclopentanone melted at 209° after two recrystallizations from ethyl alcohol.

The m.p. of this semicarbazone is also given by Venus-Danilova [4] as 209°.

Dicyclopentyl was prepared by decomposing the hydrazone of 2-cyclopentyl-cyclopentanone by Kizhner's method. Yield of hydrocarbon 92% calculated on the 2-cyclopentylcyclopentanone. The high yield of hydrocarbon was due to the introduction into the reaction of a fivefold excess of hydrazine hydrate and to prolonged heating of the reaction mixture (14 hours on water bath and 6 hours on an oil bath at bath temp. of 130-140°).

Traces of base were removed from the prepared dicyclopentyl by washing first with acetic acid and then with dilute sulfuric acid. The dried hydrocarbon distilled over metallic sodium at 188.5-189° (748 mm) and n_D^{20} 1.4650; d_4^{20} 0.8659. MR_D 44.06; calculated 43.98. Yield of dicyclopentyl 53% on the cyclopentanone taken in the reaction.

Dicyclopentyl was examined by the Raman spectrographic method. The intensity of the lines was determined visually and evaluated according to the conventional scale.

Spectrum of dicyclopentyl: 221 (0.5); 257 (1); 276 (1); 321 (9); 345 (1.5); 401 (2.5); 520 (1); 586 (1;) 701 (0); 769 (0); 793 (1.2); 839 (1); 865 (2); 893 (10; r); 963 (2); 979 (1); 1022 (5; r); 1056 (1); 1103-1107 (2.5; h); 1144 (1); 1170-1196 (2.5; d); 1275 (1.5; r); 1318 (2.5); 1364 (1.8); 1389 (1); 1445 (10); 1465 (1.5).

The spectrum of dicyclopentyl obtained in the present research agrees almost completely with the Raman spectrum obtained by Levina and co-workers [5] for dicyclopentyl prepared by the action of magnesium on cyclopentadiene hydrochloride followed by hydrogenation of the $\Delta^{2,2'}$-dicyclopentenyl.

In view of the fact that it was proposed to use in our investigation the method of catalytic dehydrogenation, it was necessary to clarify the behavior of dicyclopentyl in the conditions of this reaction. Dicyclopentyl was led over 20% platinized carbon at 300-305° without addition of hydrogen from outside. The catalyzate, obtained after the first pass, had refractive index n_D^{20} 1.4577 (original hydrocarbon had n_D^{20} 1.4650); after a second pass it had n_D^{20} 1.4518, and after a third pass n_D^{20} 1.4487. It was thus established that in the specified conditions dicyclopentyl undergoes hydrogenolysis. The same pattern of change of refractive index of dicyclopentyl was observed in the conditions of catalytic dehydrogenation by N. D. Zelinsky and I. N. Tits in the above-cited paper [2].

Isomerization of dicyclopentyl. The apparatus used was the same as in preceding researches [6]. A constant molar ratio of aluminum chloride to hydrocarbon was used in each experiment (1:3). The aluminum chloride was sublimed immediately before each experiment and did not change its external appearance during use.

Experiment 1. The reaction set in immediately after addition of the dicyclopentyl to the aluminum chloride. After 1½ minutes the temperature had risen to 100-103°, after which it began to fall gradually and 20-30 minutes later it had fallen to the original room temperature. No gaseous reaction products were evolved. After termination of the reaction, the hydrocarbon layer (89%) was decanted from the aluminum chloride, washed, dried and distilled over sodium. A portion of the reaction product was then examined by the Raman spectrographic method; another portion was subjected to fractionation and then to dehydrogenation. The data for fractional distillation are set forth in Table 1.

The constants of the obtained hydrocarbon fractions proved to be so close to the constants of dicyclopentyl and the possible products of isomerization (decahydronaphthalene and spirodecane, Table 2) that it was difficult to assess the extent of the reaction from them.

The small amount of the first fraction only permitted us to carry out the elementary analysis; this indicated that it was a product of isomerization of dicyclopentyl.

5.655 mg substance: 18.017 mg CO_2; 6.610 mg H_2O. 6.148 mg substance: 19.560 mg CO_2; 7.275 mg H_2O. Found %: C 86.91, 86.82; H 13.08, 13.24. $C_{10}H_{18}$. Calculated %: C 86.87; H 13.13.

Dehydrogenation of the second and third fractions, carried out in conditions similar to those for the dehydrogenation of dicyclopentyl, gave naphthalene.

Spectrum of product of isomerization of dicyclopentyl: 247 (0.3; r); 299 (1.5); 349 (1.5); 397 (1); 409 (12); 434 (1); 493 (5); 558 (0.5); 578 (1); 589 (0.5); 644 (0.5); 695 (1); 718 (1; d); 753 (5); 792 (0.8); 822 (0.8); 846 (4); 875 (2); 896 (0.8); 930 (0.5); 956 (0.5); 994 (2.5; r); 1040 (1); 1056 (11); 1085 (1.5; d); 1093 (0.5); 1143 (1); 1165 (5); 1196 (0.5); 1227 (2); 1256 (8); 1267 (1); 1309 (0.5); 1347 (1.5); 1356 (2.5); 1384 (1); 1443 (10); 1460 (1.5).

In the spectrum of the product of isomerization of dicyclopentyl were detected all the lines characteristic, according to Fenske [10], of trans-decahydronaphthalene. They are the strongest lines of our spectrum. The presence of weaker lines, not observed by Fenske in the spectrum of trans-decahydronaphthalene, may be explained by the limitations of Fenske's procedure which did not permit the recording of weaker lines in the spectrum. According to Fenske the strongest lines in the spectrum of cis-decahydronaphthalene are 594 (3.39); 741 (6.12); 1037 (4.66) and 1237 (4). The spectrum that we obtained contained only a weak line 1040 (1); the remaining intense lines of cis-decahydronaphthalene were not detected. This indicates the absence from our reaction product of any considerable amount of cis-decahydronaphthalene.

The most intense lines of spiro-(4,5)-decane, according to M. I. Batuev [11], are 1024 (131) and 1037 (131); medium-intensity lines are at 302 (89), 519 (81), 714 (81) and 993 (85). The lines at 299, 718, 994 and 1040 obtained in our spectrum cannot be regarded as the lines of spiro-(4,5)-decane at 302, 714 and 993 cm^{-1}, since the intense lines of spiro-(4,5)-decane at 519 and 1024 are absent.

To dicyclopentyl may belong the 896 (0.8) line whose feeble intensity suggests that dicyclopentyl is only present among the reaction products in insignificant amounts.

Consequently, from a comparison of the spectrum of the product of isomerization of dicyclopentyl with the spectra of dicyclopentyl, cis- and trans-decahydronaphthalene and spiro-(4,5)-decane it follows that the products of our reaction consist in the main of the trans form of decahydronaphthalene; spiro-(4,5)-decane is absent and dicyclopentyl is present in insignificant amount.

Experiment II. In the second experiment the reaction mixture, after the rise of temperature, was heated for 15 hours on a water bath. This enabled clarification of the influence of prolonged heating on the interaction of aluminum chloride with dicyclopentyl. The reaction products (84%) were worked up and fractionated as in the first experiment. The fractionation data are set forth in Table 1. The prolonged heating resulted in the appearance among the reaction products of a lower boiling fraction (180-182°, 9%), testifying to the more drastic modification of the molecule of dicyclopentyl. Dehydrogenation of this fraction yielded naphthalene and a very small amount of a liquid hydrocarbon which could not be examined closely.

The entire remaining product of reaction (fraction 182-186°, 83%) was converted into naphthalene on dehydrogenation. The spectrum of the product of reaction in this experiment agreed in its principal frequencies with the spectrum obtained in the first experiment, which pointed to the identity between their composition.

Experiment III was performed at a temperature not exceeding 50°. This was achieved by gradual addition of aluminum chloride to the hydrocarbon and by cooling of the reaction mixture. The reaction product (85% yield), after appropriate purification, was fractionated (Table 1). A low-boiling fraction was absent. The whole reaction product gave naphthalene on dehydrogenation.

TABLE 1

Expt. No.	Temp. of expt. (°C)	Duration of expt.	B.p. of fractions, their yield and properties						
			180-182°				182-184°		
			Yield of reaction product (%)	Content of fraction in reaction products (%)	n_D^{20}	d_4^{20}	Content of fraction in reaction products (%)	n_D^{20}	d_4^{20}
1	100-103	1-1.5 min.	89	–	–	–	3.3	1.4663	0.8648
2	100	15 hrs.	84	9.0	1.4655	0.8624	3.0	1.4660	0.8640
3	40-50	2 hrs.	85	–	–	–	1.5	1.4698	0.8671
4	0	6 hrs.	92	–	–	–	–	–	–

The data of spectrum analysis established that in the conditions of this experiment dicyclopentyl is transformed into decahydronaphthalene, predominantly the trans form.

Experiment IV was carried out for 6 hrs. at 0°. The reaction product (89% yield) distilled at 187-189° (756 mm) and had n_D^{20} 1.4700 and d_4^{20} 0.8740. In its spectrum [193 (0); 257 (1); 295 (0); 322 (8; r); 353 (1.5); 373 (1); 397 (0.3); 408 (3); 492 (2.5); 597 (3); 746 (2.5); 754 (1.5); 769 (0); 792 (1.5); 833 (0.7); 846 (2.5); 862 (0.5); 875 (1); 894 (6; r); 932 (0.5); 963 (1; h); 982 (1; h); 1016-1022 (1.5 d); 1040 (2.5); 1055 (2.5); 1070 (1); 1085 (1.5); 1107 (2; r); 1143 (1.5); 1164 (2; r); 1187 (1; h) 1241 (2); 1253 (2); 1268 (2); 1290 (0); 1317 (1.5); 1347 (1.5); 1356 (2); 1388 (0.7); 1443 (10; h); 1465 (0.8)] were detected lines characteristic of dicyclopentyl and cis- and trans-decahydronaphthalenes. Naphthalene was isolated after dehydrogenation.

Isomerization of cyclopentyl-cyclopentanol by dehydration with conc. phosphoric acid. 2-Cyclopentyl-cyclopentanol was prepared by hydrogenation of 2-cyclopentyl-cyclopentanone in presence of skeletal nickel at 200° with a hydrogen pressure of about 190 atm.

Heating of 2-cyclopentyl-cyclopentanol with a small quantity of phosphoric acid (s.g. 1.4) on an oil bath at 230-240° gave a hydrogen fraction of unsaturated character which boiled at 70-80° at 13 mm and had n_D^{20} 1.4908; d_4^{20} 0.9006. MR_D 43.72. $C_{10}H_{16}\lceil$. Calculated MR_D 43.51. Its hydrogenation over platinized carbon gave a saturated fraction from which was isolated a hydrocarbon with b.p. 186.5-187° (746 mm): n_D^{20} 1.4668; d_4^{20} 0.8665; MR_D 44.17. $C_{10}H_{18}$. Calculated MR_D 43.98. Its dehydrogenation gave a small quantity of naphthalene.

The above data provide convincing evidence of the isomerization of the dicyclopentyl system into the six-membered ring systems of octahydronaphthalene. This observation was confirmed by the measurements of the Raman spectrum.

Spectrum of product of hydrogenation: 257 (1); 299 (1.5); 321 (5); 346 (1); 408 (8); 434 (1); 494 (5); 556 (1); 592 (1.5); 695 (0.5); 746 (1); 753 (4); 792 (1); 838 (1); 845 (3); 862 (1); 875 (2); 893 (6; r); 956 (1); 963 (1); 986 (1.5; r); 1022 (2); 1056 (4); 1085 (1.2); 1100 (1.5; r); 1144 (1.5); 1165 (3); 1183 (1); 1227 (2); 1256 (3.5); 1267 (1); 1318 (1.5); 1347 (1); 1355 (2.5); 1385 (0.5); 1445 (10).

In the spectrum were detected the strongest lines of dicyclopentyl 321, 893, 1022 and 1183, and the intense lines of decahydronaphthalene 408, 494, 592, 845, 1056 and 1256.

SUMMARY

1. The product of isomerization of dicyclopentyl under the influence of aluminum chloride is a mixture of the stereoisomers of decahydronaphthalene in which the trans form predominates.

Change of temperature in the range of 0 to 100° does not influence the nature of the formed hydrocarbons.

2. The isomerization of 2-cyclopentyl-cyclopentanol on dehydration with concentrated phosphoric acid was studied. The reaction product is a mixture of cyclopentylcyclopentene and octahydronaphthalene.

3. The possibility is demonstrated of isomerization of bicyclic compounds of the cyclopentane series with ring expansion into octa- and decahydronaphthalenes.

B.p. of fractions, their yield and properties								
184-186°			186-187°			187-189°		
Content of fraction in reaction products (%)	n_D^{20}	d_4^{20}	Content of fraction in reaction products (%)	n_D^{20}	d_4^{20}	Content of fraction in reaction products (%)	n_D^{20}	d_4^{20}
88.1	1.4680	0.8667	5.6	1.4699	0.8690	–	–	–
84.0	1.4693	0.8686	–	–	–	–	–	–
81.8	1.4712	0.8688	14.0	1.4720	0.8720	–	–	–
–	–	–	–	–	–	98.0	1.4700	0.8740

TABLE 2

Hydrocarbon	B.p.	n_D^{20}	d_4^{20}	Author
Dicyclopentyl	188.5-189° (748 mm)	1.4650	0.8659	Prepared in this research
Cis-decahydronaphthalene . .	193.3°	1.4828	0.8980	Ewans [7]
	–	1.48113	0.8970	Seyer [8]
Trans-decahydronaphthalene	185.3	1.4701	0.8720	Ewans [7]
	–	1.46968	0.8700	Seyer [8]
Spirodecane	185-186° (769 mm)	1.4698	0.8766	N. D. Zelinsky and N.V. Elagina [9]

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THERMOCATALYTIC TRANSFORMATIONS OF HYDROCARBONS

I. TRANSFORMATIONS OF PHENYLCYCLOHEXANE

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Our studies of thermocatalytic transformations of aromatic hydrocarbons have shown [1] that the transformation depends on the length of the side chain and the degree of its branching at the carbon atom attached to the aromatic nucleus. In the light of these conclusions it was a matter of interest to investigate the behavior of phenylcyclohexane which contains a radical of considerable size and in which the aromatic ring is attached through a secondary carbon atom.

The synthesis of phenylcyclohexane has been described many times in the literature. It was particularly closely studied by S. S. Nametkin who thought that an analogy might be drawn between polycyclohexylbenzenes and components of petroleum lubricating oils [2]. We accomplished the synthesis of phenylcyclohexane by the action of anhydrous aluminum chloride on a mixture of benzene and chlorocyclohexane in the conditions described by N. I. Kursanov [3]. Chlorocyclohexane was obtained by interaction of cyclohexanol with gaseous hydrogen chloride on refluxing for several hours on a water bath, fresh quantities of hydrogen chloride being introduced from time to time. After heating until the separated layer of water ceased to increase in size, the reaction mixture was washed with water and weak sodium carbonate solution; the product was dried and distilled. The yield of pure chlorocyclohexane was about 75% of the theoretical; it distilled at 141-143°, d_4^{20} 1.0011. Condensation with benzene was performed in presence of 5% of anhydrous aluminum chloride; the reaction proceeded very much less intensively, however, than was reported by N. I. Kursanov and it required heating to 45-50°. The yield of phenylcyclohexane, separated by the usual methods and carefully distilled, was 55%. An additional product was dicyclohexylbenzene with b.p. 238-240°. The latest investigations have shown this to be the para-isomer and not the ortho-isomer as was suggested by N. I. Kursanov [4].

Constants of synthesized phenylcyclohexane: m.p. +6.5°, d_4^{20} 0.9445.

Found %: C 90.12; H 9.95. $C_{12}H_{16}$. Calculated %: C 90.00; H 10.00.

Various authors report d_4^{20} from 0.9436 to 0.9502, m.p. 7°.

The prepared hydrocarbon was subjected to heating with activated gumbrin in a small iron still under a reflux condenser. At the conclusion of the reaction, the mixture was freed from the formed benzene by distillation, and the residue (boiling above 150°) was extracted with ether; removal of the latter left a viscous oil which was added to the previously obtained benzene. The whole mixture was subjected to fractionation in a column.

EXPERIMENTAL

Experiment I. 100 g phenylcyclohexane and 90 g activated gumbrin were placed in a small iron still and the mixture was heated over a burner. In the first few minutes the boiling point of the mixture —determined with a thermometer whose bulb was immersed in the boiling mixture —was 210°. Then the temperature at first fell quickly and after 25 minutes it was steady at 125-130°. At this instant the condenser was moved into the sloping position and the fraction to 150° was distilled off; from the residue was obtained a substance as already described. The whole mixture was distilled, the following fractions being obtained: 1) b.p. 75-85° (12%), d_4^{20} 0.8379; 2) b.p. 85-235° (3%); 3) b.p. 235-245° (39.5%), d_4^{20} 0.9456; 4) b.p. 245-300° (9.5%); 5) b.p. above 300° (29%), d_4^{20} 0.9747. The specific gravity of the 75-85° fraction shows that it is certainly not pure benzene. The 235-245° fraction was considered to be the starting substance; the fraction above 300° partly crystallized and was purified by recrystallization from acetone to form crystals with m.p. 101-102° and molecular weight 240. Elementary analysis revealed 89.31% carbon and 10.93% hydrogen. Since dicyclohexylbenzene requires carbon 89.25% and hydrogen 10.75% with a molecular weight of 242, we are justified in regarding the prepared crystals as p-dicyclohexylbenzene, which had previously been prepared by many authors. However, not more than 10% of the total weight of the fraction boiling above 300° was obtained in the form of crystals.

Experiment II. 120 g phenylcyclohexane and 90 g activated gumbrin were heated in a small still fitted with a short column and a condenser; the volatile fractions were collected as formed, so that throughout the whole reaction period the equilibrium between dicyclohexylbenzene and benzene was being shifted; thus the experimental conditions were more drastic. The duration of the whole experiment was 2½ hours and it was stopped when the temperature in the column was 140°. The products were worked up as before and distilled to give the following fractions (table).

Boiling point (°C)	Yield (in g)	d_{20}^{20}	n_D^{20}
Up to 76	12	0.8169	1.4640
76-78	13	0.8346	1.4723
78-81	8	0.8516	1.4850
81-235	2	—	—
235-245	31	0.9458	1.5280
245-350 (8 mm)	8	—	—
210-212 (8 mm)	16	0.9798	1.5430
212 (8 mm)	6	0.9800	1.5432
212-248 (8 mm)	4.5	—	1.5450
248-250 (8 mm)	4.5	1.0020	1.5565
Above 250 (8 mm)	11	—	—
Losses	4		

Not a single one of the fractions crystallized, even after prolonged cooling to −19°. Elementary analysis of the 212° (8 mm) fraction gave:

Found %: C 89.24; H 10.82. M 238. $C_{18}H_{26}$.
Calculated %: C 89.25; H 10.75. M 242.

The refractive index of this fraction and of the adjacent ones was 1.055-1.056, which showed the identity between these fractions. In all respects the 210-212° fractions correspond to the anticipated dicyclohexylbenzene, but the latter was not, however, obtained in the crystalline form.

The 76-81° fractions, with a lower specific gravity than required for benzene, were worked up in the cold with sulfuric acid containing 5% anhydride until the reaction for benzene with formaldehyde was negative. The aniline point of the nonaromatic residue was then determined, also the aniline point of the mixture of the residue with 50% benzene. The results agreed with the aniline point of the original mixture, it being established that the latter also contained about 50% benzene. The nonaromatic residue was subjected to close fractionation to give fractions distilling between 71 and 81°. It was thus shown that the fractions are a mixture of cyclohexane and methylcyclopentane, approximately 50% of each, as evident from the following comparison:

	d_{20}^{20}	n_D^{20}
71-81° fraction	0.7654	1.4184
Pure cyclohexane	0.7815	1.4264
Pure methylcyclopentane	0.7502	1.4099
Mixture of 50% cyclohexane + 50% methylcyclopentane	0.7658	1.4181

SUMMARY

Even at low temperatures the activated clay gumbrin unusually easily transforms phenylcyclohexane into new products. The normal formation of benzene is accompanied by cleavage of cyclohexane which partially isomerizes to methylcyclopentane. A similar cleavage is known to occur with other benzene homologs containing heavy radicals (for example butylbenzene), but in the case of phenylcyclohexane the phenomenon is exceptionally pronounced. The insignificant yield of p-dicyclohexylbenzene in mild experimental conditions and the complete absence of this hydrocarbon when the reaction takes place in more drastic conditions demonstrate that in place of the anticipated p-dicyclohexylbenzene its isomerization product is formed, namely p-di-(methylcyclopentyl)-benzene, not previously described in the literature. The isomerizing action of activated clays on the cyclohexane ring is known from the literature. What is still uncertain is the degree of purity of the obtained di-(methylcyclopentyl)-benzene, since it is natural to assume that it may contain p-methylcyclopentyl-cyclohexylbenzene, likewise not described in the literature.

Conversion of the yields of products to molar ratios, assuming C_6H_{12} to be a mixture of cyclohexane and methylcyclopentane gives the following values: benzene 2.5, C_6H_{12} 1.3, $C_{18}H_{26}$ 1.0.

Consequently approximately one molecule of phenylcyclohexane splits into benzene and C_6H_{12} and two other molecules into benzene and $C_{18}H_{26}$, i.e., normal disproportionation of radicals proceeds to the extent of 66% and splitting to the extent of 34%.

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THERMOCATALYTIC TRANSFORMATIONS OF HYDROCARBONS

II. TRANSFORMATIONS OF TERT-BUTYLBENZENE

A. F. Dobryansky and E. K. Gavrilova

In a series of investigations by the authors of homologs of benzene, the transformations of methylbenzene, xylene and ethyl- and isopropylbenzenes over activated clay were studied [1]. In the present research a study was made of the behavior of an alkyl benzene in which the radical was linked to the nucleus through a quaternary carbon atom. It could be postulated for example, that tert-butylbenzene would readily undergo transformations similar to the decomposition of tert-butylphenol. Furthermore, radical-disproportionation reactions are known to occur in tertbutylbenzene under the action of anhydrous aluminum chloride. A complete analogy between aluminum chloride and activated clay has been indicated by many authors.

Tert-butylbenzene was synthesized from tert-butyl chloride and benzene with aluminum chloride as catalyst according to the general rules for this type of synthesis. The prepared hydrocarbon boiled at 168-170° and had d_4^{20} 0.8649 and n_D^{20} 1.4919 (the corresponding literature values are 0.8669 and 1.4925).

Thermal catalysis was performed in an iron still with an equal weight of activated gumbrin. From the very start of the experiment the boiling point of the mixture was 130° and after 2 hours the temperature was constant at 120.5°. After working up of the mixture in the usual manner [2], distillation gave the following fractions (see table).

B.p.	Yield (in g)	d_4^{20}	n_D^{20}
79- 85°	11.5	0.8744	1.5000
85-165	1.5	–	–
165-169	38.6	0.8608	1.4921
169-173	0.6	–	–
173-220	8.2	0.8612	1.4897
220-227	6.6	–	–
227-232	9.1	Crystals	–
Residue	3.7		

Elementary analysis of the 227-232° fraction gave: C 88.20% and H 11.80%. The theoretical values for ditert-butylbenzene are %: C 88.34; H 11.66.

Cryoscopic determination of the molecular weight gave (average of four determinations) 181.2 (calcd. 190.1). M.p. 76-77° (in a sealed capillary) (the literature gives 76°).

All these data definitely point to the formation of p-ditert-butylbenzene as a result of the thermocatalytic transformation. Oxidation of this hydrocarbon with potassium permanganate and, in another experiment, with chromic acid mixture did not give any results due in part to the high volatility of the hydrocarbon which sublimed from solutions into the neck of the flask.

The molar ratios between benzene and ditert-butylbenzene are 1.2: 1; consequently, rather more benzene than was to be expected had formed; and since the transformation was not accompanied by formation of trisubstituted products, evidently due to steric hindrance, the slight excess of benzene must have been the result of radical cleavage apart from disproportionation.

It is interesting that about 40% of butylbenzene was recovered unchanged, which is considerably less than, for example, in the transformation of ethylbenzene in similar conditions. Only at 300° and with heating of the ethylbenzene for 30 hours in an autoclave is the amount of recovered ethylbenzene about 40%. The far-reaching transformation of tert-butylbenzene at low temperatures is comparable only with the transformation of isopropylbenzene or phenylcyclohexane.

SUMMARY

Substitution of a hydrogen atom in benzene by a radical to the ring through a quaternary carbon atom creates instability of the bond between the radical and the benzene ring, due to which the latter undergoes cleavage with extraordinary ease. Consequently the presence of tert-butylbenzene in petroleum appears highly improbable.

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* See Consultants Bureau Translation, p. 1167.

CONJUGATED SYSTEMS

XLIX. THE PROBLEM OF THE ORDER OF ADDITION OF ALKYL HYPOHALITES TO TERTIARY VINYLACETYLENIC ALCOHOLS

A. A. Petrov, E. S. Bravo, V. V. Davidovich, O. S. Dyatkova and G. V. Kuznetsova

The study of the mutual influence of the double and the triple bond in the reactions of vinylacetylenic compounds with halogens, hydrogen halides and hypohalites offers undoubted interest for the theory of organic chemistry since it throws light on many unsolved problems of the chemistry of unsaturated compounds.

In previous papers it was shown that vinylacetylene adds on bromine at all three possible positions, but the 1,2-product predominates [1]. Hydrogen halides give, depending on the conditions, 1,2- and 1,4-products in various ratios [2-4]. No trustworthy study has hitherto been made of the order of addition of hypohalogen compounds.

Homologs of vinylacetylene with a radical in the 1-position add on bromine [5], and alkyl hypohalites preferentially add on at the double bond (in the 3,4-position). On the other hand with hydrogen halides in presence of Cu_2Halg_2 they give 1,2-products [7].

This variation in the order of addition of halogens, hypohalites and hydrogen halides to α-alkyl-substituted vinylacetylenes calls for thorough investigation and clarification.

We therefore undertook the investigation of the addition of electrophilic agents to other vinylacetylenic compounds and in particular to the readily accessible tertiary vinylacetylenic alcohols. A point of special interest was the establishment of whether addition here took place at the double bond.

In recent years the chemistry of the vinylacetylenic alcohols has been the subject of extensive investigations by I. N. Nazarov [8] and other chemists. On the problem of interest to us, however, the literature is entirely lacking in data. In the first place we attempted to determine the order of addition to tertiary vinylacetylenic alcohols of alkyl hypoiodites. The experiments were performed in the usual conditions repeatedly employed by one of us for the synthesis of β-iodoethers [9].

Investigations were made on 9 tertiary alcohols whose formulas are listed in the table.

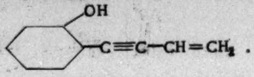
Addition of methyhypoiodite to vinylacetylenic alcohols would be expected to yield 6 substances. Since the reaction products failed to distil without decomposition in the vacuum attainable by us (2 mm), and since we were mainly interested in the tendency of these substances to add on alkyl hypohalites to the vinyl grouping, we did not isolate the iodoethers but worked up the reaction mixture with alcoholic alkali. In this process, only one of the possible products of addition of alkyl hypohalites to tertiary vinylethinyl carbinols was bound to undergo cleavage with formation of alkoxy derivatives of vinylacetylene (previously studied by one of us [10]) according to the scheme:

$$R_2C(OH)-C\equiv C-CH(OR)-CH_2I \longrightarrow R_2C(OH)-C\equiv C-C(OR)=CH_2 \longrightarrow$$

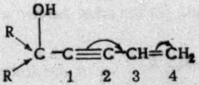
$$\longrightarrow HC\equiv C-C(OR)=CH_2+R_2C=O.$$

Experiments showed that all the substances enumerated in the table, with exception of 8 and 9, give alkoxyvinylacetylenes as a result of the above-formulated transformations, and accordingly they add on alkyl hypoiodites to a considerable extent at the double bond. The yield of alkoxyvinylacetylenes, and consequently also the relative yield of 3,4-products, increases with the number of radicals in the tertiary alcoholic grouping. Thus, whereas in the case of dimethylvinylethinyl carbinol the yield of methoxyvinylacetylene is 18%, in similar conditions in the case of methyl-tert-butylcarbinol the yield of methoxyvinylacetylene is already 36%. When the radicals are attached to a cyclic system the yield is slightly lowered.

It is possible that these data are evidence of the spatial character of the influence of radicals on the order of addition of alkyl hypoiodites: the complexity of the radical in the 1-position hinders the attack of iodine and thereby favors 3,4-addition. Another possibility is the electronic influence of accumulation of methyl groups in the conjugated

Starting substance		Iodoether			
Expt. No.	Formula	Taken (g)	Yield of crude product (in g)	% I	
				Found	Calc.
1	$(CH_3)_2C(OH)-C\equiv C-CH=CH_2$	55	98.4	44.02	46.99
2	$(CH_3)(C_2H_5)C(OH)-C\equiv C-CH=CH_2$	51	88.3	42.80	44.66
3	$(CH_3)[(CH_3)_3C]C(OH)-C\equiv C-CH=CH_2$.	51	80.0	37.53	40.92
4		62	100.0	38.18	41.19
5	$(CH_3)(C_6H_5)C(OH)-C\equiv C-CH=CH_2$.	50	85.5	35.82	38.44
6	$(CH_3)(CH_3C_6H_4)C(OH)-C\equiv C-CH=CH_2$	32	45.0	36.46	36.87
7	$(C_6H_5)_2C(OH)-C\equiv C-CH=CH_2$	42	60.0	29.12	32.36
8	$(CH_3)(C_2H_5OC_6H_4)C(OH)-C\equiv C-CH=CH_2$	48	64.0	40.62	33.92
9	$[(CH_3)_2NC_6H_4]_2C(OH)-C\equiv C-CH=CH_2$	50	Not determined		

system; such an accumulation must increase the activity of the vinyl grouping in accordance with the scheme:



Replacement of one alkyl radical by an aryl increases the yield of methoxyvinylacetylene.

The products of interaction of vinylethinylcarbinols 8 and 9 with iodine and mercuric oxide did not give any enynic ether. In place of the latter a small amount of vinylacetylene was obtained. The reason for this may be that the original carbinol was iodinated in the course of the reaction but did not add on alkyl hypoiodite (due to the presence of groups facilitating the entry of halogen into the ring). Other special properties of these alcohols may here come into play, particularly the exceptional susceptibility to dehydration and polymerization under the influence of iodine.

The tertiary alcohol obtained from vinylacetylene and Michler's ketone requires further study; under the action of acid it readily forms a green dye with the vinylacetylenic residue. The yield of enynic ether may be only a relative index of the direction of the reaction. 3,4-Products undoubtedly give enynic ethers not in theoretical amounts under the action of caustic alkalies. Since here we have two stages of reaction and in each stage the yield can hardly exceed 70%, the yield of enynic ether cannot exceed 50%. If this circumstance is taken into consideration, we may conclude that 1,2-addition is nearly always the main direction of the reaction of alkyl hypoiodites with tertiary vinylethinylcarbinols. The ethylenic bond is more reactive than the acetylenic, evidently because of the influence of the radicals in the 1-position. Hydroxyl, however, possibly weakens this influence due to which the addition does not proceed only in the 3,4-position.

EXPERIMENTAL

1. Preparation of Tertiary Vinylacetylenic Alcohols

The first four of the alcohols listed in the table were prepared by A. E. Favorsky's method by the action of powdered alkali on a mixture of vinylacetylene and the appropriate ketone in an ethereal medium. The remaining alcohols were prepared by the Grignard synthesis: the action of the respective ketones on an ethereal solution of vinylethinylmagnesium bromide. The tertiary alcohols prepared from methyl-p-tolyl ketone, methylphenethyl ketone and Michler's ketone are here described for the first time. Their constants are set forth below. The constants of all the other alcohols did not differ substantially from those found by I. N. Nazarov [11], and they are therefore omitted here.

For preparation of methyl-p-tolyl-vinylethinylcarbinol, 45 g methyl-p-tolyl ketone in 100 ml ether was added with cooling and stirring to an ethereal solution of vinylethinylmagnesium bromide prepared from 10 g

Max. yield on I content (in %)	Iodine split off (%)	Yield of methoxyvinylacetylene	Yield of ketone (%)
75.2	81.3	18.0	Not isolated
72.8	88.0	22.1	Not isolated
74.2	89.0	35.9	55
72.9	88.3	19.0	40
75.0	88.3	40.1	57
75.9	96.3	27.1	52
76.7	97.1	26.5	Not isolated
–	98.6	Absent	
		Absent	

magnesium. The following day the mixture was worked up under cooling with ice and saturated ammonium chloride solution. The yield of alcohol was 70%.

Methyl-p-tolyl-vinylethinylcarbinol is a viscous liquid with the odor characteristic of all the alcohols of this series.

B.p. 144-145° at 10 mm, d_4^{20} 1.0043, n_D^{20} 1.5328. MR_D Found 58.88. $C_{13}H_{14}O$. Calculated 57.69.

15.80 mg substance: 48.46 mg CO_2; 10.93 mg H_2O. Found %: C 83.70; H 7.74. $C_{13}H_{14}O$. Calculated %: C 83.83; H 7.58.

By the same method, starting from 37 g crystalline methyl-p-phenethyl ketone, the preparation was carried out of methyl-p-phenethyl-vinylethinylcarbinol in 65% yield. A viscous oil with b.p. 166-169° at 10 mm, d_4^{20} 1.0450, n_D^{20} 1.5503. MR_D Found %: 66.01. $C_{14}H_{16}O_2$. Calculated 63.95.

12.14 mg substance: 34.48 mg CO_2; 8.22 mg H_2O. Found %: C 77.51; H 7.58. $C_{14}H_{16}O_2$. Calculated %: C 77.75; H 7.46.

When preparing the alcohol from Michler's ketone it was necessary to take a considerable quantity of ether for dissolving the ketone. Methyl-p-dimethylaminophenylvinylethinylcarbinol crystallized from ether in the form of a colorless substance, readily changing to green when kept.

2. Action of Iodine and Mercuric Oxide on a Solution of Dimethylvinylethinylcarbinol in Methyl Alcohol*

To a solution of 112 g dimethylvinylethinylcarbinol (30% excess) in 180 ml methanol was added 120 g mercuric oxide; then at 20-25° (water cooling) and with mechanical stirring was introduced 200 g pulverized iodine in small portions over a period of 4 hours. At the conclusion of the reaction, the precipitate of mercuric oxide and mercuric iodide was filtered off and washed on the filter with alcohol; the filtrate was diluted with water. The oil which came down was washed with water and dried with calcium chloride. Yield 185 g of a substance (88% calculated on the iodine) which was treated with alkali without further purification.

185 g of the iodoether was added to a solution (heated on the water bath) of 60 g KOH in 150 ml ethanol, after which the mixture was boiled for another 45 minutes. To the mixture was then added 500 ml water and distillation was carried out in a column. Dilution of the distillate with water caused the methoxyvinylacetylene to separate. The aqueous layer was subjected to a second distillation and a further crop of methoxyvinylacetylene was separated from the first portions. This treatment of the distillates was repeated several times.

The methoxyvinylacetylene was washed twice with conc. calcium chloride solution and distilled in a column. A total of 11.5 g methoxyvinylacetylene was obtained, equivalent to a yield of 20% calculated on the iodoether. Constants found for methoxyvinylacetylene: b.p. 86-87.5°, d_4^{20} 0.8697, n_D^{20} 1.4434. Pure methoxyvinylacetylene prepared by another method [10] had: b.p. 86.5° at 752 mm, d_4^{20} 0.8712, n_D^{20} 1.4446.

3. Action of Iodine and Mercuric Oxide on a Solution of Dimethylvinylethinylcarbinol in Ethyl Alcohol

In the above-described conditions, 66 g dimethylethinylcarbinol (50% excess) in 150 ml ethyl alcohol and 100 g iodine gave 69 g iodoether. Yield 69%. Dehalogenation of this ether gave 7.8 g ethoxyvinylacetylene with b.p. 102-104°, d_4^{20} 0.8541 and n_D^{20} 1.4440. Yield 25%. Constants of pure ethoxyvinylacetylene prepared by another method [10] were: b.p. 103.4-103.7° at 752 mm, d_4^{20} 0.8570, n_D^{20} 1.4432.

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* This experiment (and the experiment following) were performed by A. A. Petrov in 1944.

4. Comparative Experiments on the Action of Iodine and Mercuric Oxide in Methanol on Tertiary Vinylethinylcarbinols

To a solution of the vinylethinylcarbinol in an 8-10 fold excess of methanol was added mercuric oxide (50% excess), and, with intensive stirring and at 10-15°, the calculated amount of powdered iodine in small portions. Addition of the iodine required about 1½ - 2 hours. At the conclusion of the reaction the solution was separated from the excess of mercuric oxide and mercuric iodide, and its amount was measured. The amount of iodoether was determined separately on a sample. This was done by diluting the sample with water, extracting the resultant oil with ether, washing the ethereal solution with saturated calcium chloride solution to remove alcohol, and then evaporating the ether in vacuum (2 mm). The residue was weighed and its content of iodine was determined. In some cases the content of methoxyl groups was also determined (Zeisel method). The calculated amounts of iodoethers, based on the iodine and methoxyl group contents, were in good agreement.

Results of analysis of the iodoethers for content of iodine are given in the table. Here we only present the analytical data (Zeisel) for two substances (3 and 5).

For iodoether 3: 0.1762 g substance: 0.1262 g AgI. Found %: CH_3O 9.47. $C_9O_{15}OIOCH_3$.
Calculated %: CH_3O 10.01.

For iodoether 5: 0.1826 g substance: 0.1233 g AgI. Found %: CH_3O 8.93. $C_{12}H_{15}OIOCH_3$.
Calculated %: CH_3O 9.40.

The main bulk of the solution was worked up with a twofold excess of KOH and separation of methoxyvinylacetylene was effected from the obtained mixture, using the method described in experiment 3; the product was distilled from a small Favorsky flask. The 85-88° fraction was weighed. In the majority of cases the whole of the material distilled over in this range. The iodine ion content of the residue was determined.

The ketones were isolated from the reaction mixture by prolonged steam distillation or by extraction with ether. Their constants corresponded to the literature values. Thus, for example, for pinacoline the values found were: b.p. 103-106°, d_4^{20} 0.8055, n_D^{20} 1.3985. Literature data [12]: b.p. 103-106°, d_4^{16} 0.7999. For acetophenone was found: b.p. 200-202°, d_4^{20} 1.0288; n_D^{20} 1.5322. Literature data [12]: b.p. 202°, d_4^{20} 1.0236, n_D^{20} 1.5342.

The purest preparations of methoxyvinylacetylene were obtained from those carbinols from which are formed ketones nonvolatile in steam, for example from diphenylvinylethinylcarbinol (b.p. 86-87°, d_4^{20} 0.8702, n_D^{20} 1.4440).

SUMMARY

1. An investigation was made of the order of addition of methyl hypoiodite to 9 tertiary dialkyl-, alkylaryl-, and diaryl-vinylethinylcarbinols, as well as of the order of addition of ethyl hypoiodite to dimethylvinylethinylcarbinol.

2. It was established that alkyl hypoiodites add on to a considerable extent in the 3,4-position (at the ethylenic bond).

3. Alkaline cleavage of the reaction products gave methoxy- and ethoxyvinylacetylenes.

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* See Consultants Bureau Translation, p. 745.

SYNTHESIS OF HYDROCARBONS

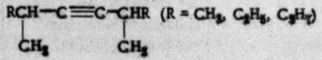
XLI. DIISOBUTYLACETYLENE AND DIISOAMYLACETYLENE

R. Ya. Levina, V. V. Ershov and Yu. S. Shabarov

In our preceding communications a new method was described for the synthesis of normal and iso dialkylacetylenes with a central triple bond.

Dialkylacetylenes with a normal structure (I) were synthesized by reaction of organomagnesium compounds with a diprimary acetylenic 1,4-dichloride of the propargyl type – 1,4-dichloro-2-butyne [1,2].

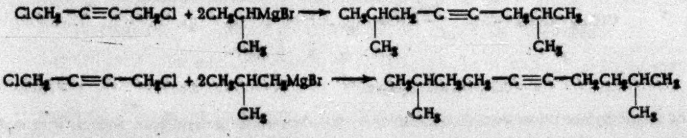
The reaction of methylmagnesium bromide (or iodide) with homologs of 1,4-dichloro-2-butyne (disecondary acetylenic 1,4-dichlorides) was the method used for synthesis of not previously described dialkylacetylenes containing two branched groupings in the α-position to the triple bond: diisopropylacetylene [3], disecondary butylacetylene and disecondary amylacetylene [4]:



$$\underset{CH_3}{RCH}-C\equiv C-\underset{CH_3}{CHR} \quad (R = CH_3,\ C_2H_5,\ C_3H_7)$$

In the present research we studied the possibility of employing 1,4-dichloro-2-butyne as the starting material for synthesis of dialkylacetylenes with an iso structure and a central triple bond as well as two branches in the β- and in the γ-position to the triple bond.

It was established that reaction of isopropylmagnesium bromide and isobutylmagnesium bromide with 1,4-dichloro-2-butyne gave, respectively, 2,7-dimethyl-4-octyne (nor previously described in the literature) and 2,9-dimethyl-5-decyne*(yield 5% of the theoretical):



$$ClCH_2-C\equiv C-CH_2Cl + 2CH_3\underset{CH_3}{CHMgBr} \rightarrow CH_3\underset{CH_3}{CH}CH_2-C\equiv C-CH_2\underset{CH_3}{CH}CH_3$$

$$ClCH_2-C\equiv C-CH_2Cl + 2CH_3\underset{CH_3}{CH}CH_2MgBr \longrightarrow CH_3\underset{CH_3}{CH}CH_2CH_2-C\equiv C-CH_2CH_2\underset{CH_3}{CH}CH_3$$

The structure of the prepared alkynes was demonstrated by oxidation to the corresponding acids – isovaleric and isocaproic acids (identified by the melting points of the anilides).

The simplicity of the synthesis (in the usual conditions of the Grignard reaction) and the fewness of the stages permit this method to be recommended for preparation of the previously inaccessible dialkylacetylenes with an iso structure, a central triple bond and two branched (methyl) groups at various distances from the triple bond. The yields of these hydrocarbons, however, are low.

Comparison of the physical properties of the dialkylacetylenes synthesized by us in the present and the preceding [1-4] researches showed that these compounds are characterized by exaltation of molecular refraction on transition from hydrocarbons with a normal structure to those which are symmetrically branched, as well as on progressive approach of both branches to the triple bond (Table 1).

When performing the reactions between isopropyl- and isobutylmagnesium bromides and dichlorobutyne, the processes that took place were similar to those observed by us in preceding investigations [2,4]. Thus, on fractionation in a column of the products of both reactions, separation was effected of the conjugated dienic hydrocarbons (not described in the literature): 2,3-diisopropyl-1,3-butadiene and 2,3-diisobutyl-1,3-butadiene (yield

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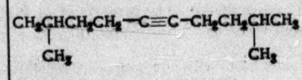
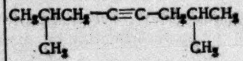
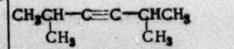
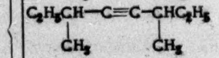
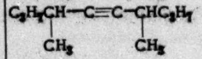
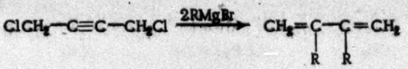
* From the product of reaction between acetylene dimagnesium bromide and isoamylbromide M. S. Malinovsky [5] isolated, 2,9-dimethyl-5-decyne, which distilled over the range of 200-212°.

TABLE 1

Exaltation of Molecular Refraction of Dialkylacetylenes

Branch	Formula	Name	EM_D^*	Literature references
None	$C_2H_5-C\equiv C-C_2H_5$	3-Hexyne(diethylacetylene)	0.21	[1]
	$C_3H_7-C\equiv C-C_3H_7$	4-Octyne(dipropylacetylene)	0.42	[2]
	$C_4H_9-C\equiv C-C_4H_9$	5-Decyne(dibutylacetylene)	0.39	[2]
	$C_5H_{11}-C\equiv C-C_5H_{11}$	6-Dodecyne(diamylacetylene)	0.41	[2]
In the γ-position to the triple bond	 $CH_3\underset{CH_3}{CH}CH_2CH_2-C\equiv C-CH_2CH_2\underset{CH_3}{CH}CH_3$	2,9-Dimethyl-5-decyne-(diisoamylacetylene)	0.55	Prepared in this research
In the β-position to the triple bond	 $CH_3\underset{CH_3}{CH}CH_2-C\equiv C-CH_2\underset{CH_3}{CH}CH_3$	2,7-Dimethyl-4-octyne-(diisobutylacetylene).	0.76	
In the α-position to the triple bond	 $CH_3\underset{CH_3}{CH}-C\equiv C-\underset{CH_3}{CH}CH_3$	2,5-Dimethyl-3-hexyne-(diisopropylacetylene)	0.92	[3,4]
	 $C_2H_5\underset{CH_3}{CH}-C\equiv C-\underset{CH_3}{CH}C_2H_5$	3,6-Dimethyl-4-octyne-(disec-butylacetylene)	0.92	[4]
	 $C_3H_7\underset{CH_3}{CH}-C\equiv C-\underset{CH_3}{CH}C_3H_7$	4,7-Dimethyl-5-decyne-(disec-amylacetylene)	1.04	[4]

5-6% of the theoretical), whose formation is explained by a twofold allylic rearrangement of the dichlorobutyne in the instant of reaction [1]:



$$ClCH_2-C\equiv C-CH_2Cl \xrightarrow{2RMgBr} CH_2=\underset{R}{C}-\underset{R}{C}=CH_2$$

R = C_3H_7-iso and C_4H_9-iso

The isolated dienic hydrocarbons were characterized by the preparation of crystalline adducts with maleic anhydride [6].

In comparison with many conjugated dienic hydrocarbons, 2,3-diisopropyl-1,3-butadiene and 2,3-diisobutyl-1,3-butadiene have lower constants and a considerably lower exaltation of molecular refraction than those characterizing homologs of 1,3-butadiene with free methylene groups at the ends of the conjugated system: ($CH_2=C(R)-CH=CH_2$ and $CH_2=C(R)-C(R)=CH_2$).

TABLE 2

Dienic hydrocarbons	EM_D	
	R = CH_3	R = C_3H_7-iso
$R-CH=CH-CH=CH_2$	1.55 [7]	1.81 [8]
$CH_2=C(R)-CH=CH_2$	1.00 [7]	0.69 [9]
$CH_2=C(R)-C(R)=CH_2$	0.77 [10]	0.26 (our research)

Table 2 contains some examples illustrative of this characteristic change of exaltation of molecular refraction of conjugated dienes in dependence on the position of the alkyl groups.

A second side reaction — the formation of alkanes from radicals of organomagnesium compounds under the action of 1,4-dichloro-2-butyne —

$ClCH_2-C\equiv C-CH_2Cl + 2RMgBr \rightarrow R-R + 2MgBrCl + (-CH_2C\equiv C-CH_2-)_x$, where R = C_3H_7-iso and C_4H_9-iso.

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* The molar refractions were calculated by the usual method: summation of the atomic refractions and the increment of the triple bond.

gave lower yields (5 and 10% of the theoretical) of the respective alkanes (R—R) than when using unbranched alkylmagnesium halides [2].

EXPERIMENTAL

Synthesis of Diisobutylacetylene (2,7-Dimethyl-4-octyne)

To isopropylmagnesium bromide (105 g isopropyl bromide, 20 g magnesium and 225 ml absolute ether) was slowly added, with continual stirring and periodic cooling with water, an ethereal solution (1:1 by volume) of 1,4-dichloro-2-butyne (b.p. 75° at 28 mm; 41 g; 1/3 mole). The reaction mixture was stirred for a further 3 hours at room temperature; decomposition was effected on the following day with dilute 2 N acetic acid. Another four experiments were carried out in similar conditions. The ether was distilled off from the washed and dried ethereal extracts and the residue distilled to give two broad cuts with b.p. 42-70° (761 mm) and 44-80° (25 mm).

The 42-70° fraction was freed from traces of halide by treatment with sodium in liquid ammonia; it was then distilled in a column (50 theoretical plates) to give 5 g (5% of the theoretical reckoned on the 1,4-dichloro-2-butyne) 2,3-dimethylbutane (diisopropyl): b.p. 56.5-57° (755 mm); n_D^{20} 1.3755; d_4^{20} 0.6595.

Literature data: b.p. 57.9° (760 mm); n_D^{20} 1.3722; d_4^{20} 0.6615 [11].

The 44-80° (25 mm) fraction was heated with sodium and distilled over sodium. It was then fractionally distilled in a column (50 theoretical plates) to give two isomeric hydrocarbons: 2,3-diisopropylbutadiene-1,3 (9.5 g, 5.5% of the theoretical) and 2,7-dimethyl-4-octyne (8 g, 5% of the theoretical, reckoned on the dichlorobutyne).

2,3-Diisopropyl-1,3-butadiene (not described in the literature):

B.p. 145.5-146° (744 mm); n_D^{20} 1.4400; d_4^{20} 0.7639; MR_D 47.70; $C_{10}H_{18}\Gamma_2$. Calculated: MR_D 47.44; EM_D 0.26.

Found %: C 86.68, 86.77; H 13.30, 13.22. $C_{10}H_{18}$. Calculated %: C 86.94; H 13.06.

2,3-Diisopropylbutadiene readily entered into reaction with maleic anhydride (on brief heating without a solvent); the adduct had m.p. 118°, and its analysis corresponded to the composition $C_{14}H_{20}O_3$.

Found %: C 71.10, 70.99; H 8.62, 8.51. Calculated %: C 71.14; H 8.39.

2,7-Dimethyl-4-octyne (diisobutylacetylene; not described in the literature):

B.p. 158-158.5° (748 mm); n_D^{20} 1.4328; d_4^{20} 0.7619; MR_D 47.14. $C_{10}H_{18}\digamma$. Calculated: MR_D 46.38; EM_D 0.76.

Found %: C 86.96, 86.79; H 13.24, 13.26. $C_{10}H_{18}$. Calculated %: C 86.94; H 13.06.

Oxidation of the isolated 2,7-dimethyl-4-octyne (5.4 g) with 68% nitric acid (9 ml) in presence of mercuric nitrate (0.2 g) led to formation of only isovaleric acid with b.p. 175-178° at 757 mm (2.7 g, 33.7% of the theoretical); m.p. of the anilide 110°; a mixed melting test with the anilide of authentic isovaleric acid did not give a depression of melting point.

Literature data for isovaleric acid [12]: b.p. 176° (760 mm); anilide, m.p. 109°.

Synthesis of Diisoamylacetylene (2,9-Dimethyl-5-decyne)

The reaction between isobutylmagnesium bromide (20 g magnesium, 125 g isobutyl bromide and 225 ml absolute ether) and 1,4-dichloro-2-butyne (41 g, 1/3 mole) was performed by the above-described procedure. Vacuum distillation of the product of reaction (from five experiments) gave two broad fractions: 1) b.p. 40-80° (145 mm) and 2) b.p. 50-100° (25 mm).

The lower boiling fraction was freed from traces of halide by the action of sodium in liquid ammonia; distillation in a column with 50 theoretical plates gave 16 g (10% of the theoretical reckoned on the dichlorobutyne) 2,5-dimethylhexane:

B.p. 107.8-108° (751 mm); n_D^{20} 1.3940; d_4^{20} 0.6981.

Literature data [13]: b.p. 109.3° (760 mm); n_D^{20} 1.3930; d_4^{20} 0.6949.

The 50-100° (25 mm) fraction was vacuum-fractionated in a column to give 2,3-diisobutyl-1,3-butadiene (10.4 g, 4.2% of the theoretical) and 2,9-dimethyl-5-decyne (12.5 g, 5% of the theoretical calculated on the initial dichlorobutyne).

2,3-Diisobutyl-1,3-butadiene (not described in the literature):

B.p. 75° (19 mm); n_D^{20} 1.4452; d_4^{20} 0.7766; MR_D 57.14. $C_{12}H_{22}\ulcorner_2$. Calculated: MR_D 56.68; EM_D 0.46.

Found %: C 86.49, 86.68; H 13.44, 13.24. $C_{12}H_{22}$. Calculated %: C 86.66; H 13.34.

2,3-Diisobutylbutadiene reacts readily with maleic anhydride (under the same conditions as in the case of 2,3-diisopropylbutadiene-1,3). The adduct has melting point 64°, its analysis corresponding to $C_{16}H_{24}O_3$.

Found %: C 72.81, 72.65; H 9.09, 9.23. $C_{16}H_{24}O_3$. Calculated %: C 72.69; H 9.15.

2,9-Dimethyl-5-decyne (diisoamylacetylene): b.p. 91.9° (19 mm); n_D^{20} 1.4398; d_4^{20} 0.7814; MR_D 56.16. $C_{12}H_{22}\ulcorner^{\equiv}$. Calculated MR_D 55.61; EM_D 0.55.

Found %: C 86.83, 86.79; H 13.22, 13.27. $C_{12}H_{22}$. Calculated %: C 86.66; H 13.34.

Literature data [5]: b.p. 200-212°; n_D^{20} 1.4315; d_4^{17} 0.795.

Oxidation of 2,9-dimethyl-5-decyne (3.6 g) in the conditions outlined above gave only isocaproic acid with b.p. 192-194° at 760 mm (1.5 g, 30% of the theoretical). The anilide melts at 112°. The anilide which we specially synthesized from isocaproic acid had m.p. 111°; m.p. of mixed specimen 111-112°.

Literature Data for isocaproic acid [12]: b.p. 195°, anilide, m.p. 111°.

The structure of 2,9-dimethyl-5-decyne and 2,7-dimethyl-4-octyne was confirmed by the presence of the characteristic frequencies of the triple bond in their Raman spectra. This optical investigation* also showed that the alkynes synthesized by us did not contain admixtures of alkenes or alkadienes.

SUMMARY

1. A study was made of the reaction between 1,4-dichlorobutyne and alkylmagnesium bromides containing a branched radical —isopropyl —and isobutylmagnesium bromides.

2. It was shown that the reaction proceeds in three directions: with formation of dialkylacetylenes with a symmetrically branched structure (normal reaction products), 2,3-dialkyl-1,3-butadiene (resulting from a twofold allylic rearrangement of the initial dichlorobutyne in the instant of reaction), and alkanes (formed by dimerization of the radicals of the organomagnesium compound).

3. Products synthesized for the first time were 2,3-diisopropylbutadiene-1,3, 2,3-diisobutyl-1,3-butadiene, 2,7-dimethyl-4-octyne (diisobutylacetylene). 2,9-Dimethyl-5-decyne- (diisoamylacetylene) was obtained with more accurate constants than those reported in the literature.

4. The structure of 2,7-dimethyl-4-octyne and 2,9-dimethyl-5-decyne was confirmed by their oxidation to isovaleric and isocaproic acids, which were characterized as their crystalline anilides.

5. The structure of both the diene hydrocarbons was confirmed by the preparation of the products of their addition to maleic anhydride (not described in the literature).

6. It was shown that the exaltations of the molecular refractions of symmetrical acetylenic hydrocarbons with a central triple bond increase on transition from hydrocarbons with a normal structure to those with symmetrical branches and on approach of both branches to the triple bond.

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* The Raman spectra of our synthesized hydrocarbons were investigated by P. A. Akishin and will be described in a separate communication.

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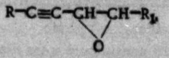
OXIDATION OF VINYLACETYLENIC HYDROCARBONS BY ORGANIC HYDROPEROXIDES

1. OXIDATION OF 4-PHENYLETHINYL-3-HEPTENE BY ACETYL HYDROPEROXIDE

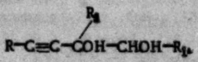
N. M. Malenok and I. V. Sologub

It has been established that the oxidation of vinylacetylenic hydrocarbons of various structures by acetyl hydroperoxide proceeds at the double bond with formation of acetylenic oxides (I) [1-4]:

I. 

$$R-C\equiv C-\underbrace{CH-CH}_{O}-R_1,$$

but sometimes glycols (II) and mono- and diacetates of unsaturated hydrocarbons are obtained [5, 6]; these are secondary products formed from the oxides:

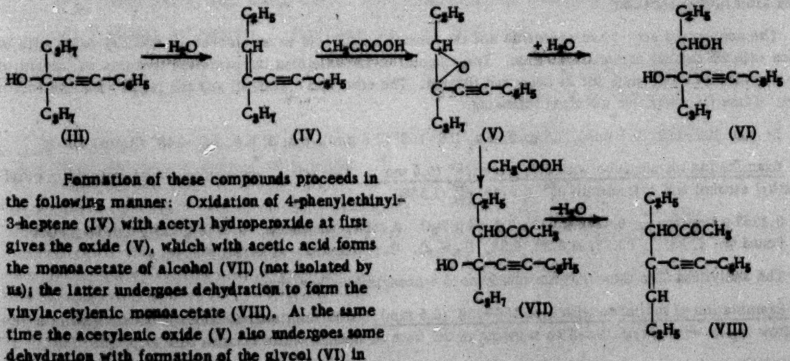
II. 

$$R-C\equiv C-\overset{R_2}{C}OH-CHOH-R_1.$$

Similar results were obtained by other authors [7, 8, 9, 10] on oxidation of various unsaturated hydrocarbons with organic hydroperoxides.

When the oxide ring is formed with two secondary carbon atoms, the resultant acetylenic oxide is stable and can be easily isolated; but an oxide ring with a secondary and a tertiary carbon atom is unstable and in the process of formation and separation it readily undergoes acetylation and hydration.

In the present research we aimed at confirming this behavior by oxidizing (with acetyl hydroperoxide) a vinylacetylenic hydrocarbon — 4-phenylethinyl-3-heptene (IV) — whose structure differed from that of the previously oxidized unsaturated hydrocarbons. The starting substance for this hydrocarbon was the acetylenic alcohol 4-phenylethinyl-heptan-4-ol (III) which was prepared by Zh. I. Iotsich's method from phenylacetylene and dipropyl ketone. The alcohol was then dehydrated with acetic anhydride to form the unsaturated hydrocarbon. Its oxidation with acetyl hydroperoxide led to isolation of three products: an oxide, 4-phenylethinyl-3-heptene (V); an acetylenic glycol, 4-phenylethinylheptane-3, 4-diol (VI); and a vinylacetylenic monoacetate, 4-phenylethinyl-5-acetylhydroxy-3-heptene (VIII):



Formation of these compounds proceeds in the following manner: Oxidation of 4-phenylethinyl-3-heptene (IV) with acetyl hydroperoxide at first gives the oxide (V), which with acetic acid forms the monoacetate of alcohol (VII) (not isolated by us); the latter undergoes dehydration to form the vinylacetylenic monoacetate (VIII). At the same time the acetylenic oxide (V) also undergoes some dehydration with formation of the glycol (VI) in which the presence of the triple bond was demonstrated by quantitative bromination.

EXPERIMENTAL

Synthesis of 4-Phenylethinylheptan-4-ol

100 g phenylacetylene (b.p. 143 - 145° at 738 mm) was condensed by the Iotsich reaction with 111 g dipropyl ketone (b.p. 140 - 142° at 744 mm); a liquid mass was obtained, from which three fractional distillations yielded 140 g light-yellow liquid with b.p. 119 - 120° at 0.5 mm. Yield 66.1%, reckoned on the phenylacetylene.

d_{20}^{20} 0.9487; n_D^{20} 1.5330; MR_D 70.69; calculated 67.39.

0.1194 g substance: 0.3663 g CO_2; 0.1058 g H_2O. 0.1238 g substance: 0.3800 g CO_2; 0.1062 g H_2O. 0.1142 g substance: 12.25 ml CH_4 (19.5°, 737.5 mm). 0.3499 g substance; 27.75 g C_6H_6; Δt 0.31°. Found %: C 83.67, 83.69; H 9.84, 9.53; OH 7.4; M 209.0. $C_{15}H_{20}O$. Calculated %: C 83.27; H 9.33; OH 7.9; M 216.1.

The prepared alcohol dissolved readily in ethyl alcohol, ethyl ether, chloroform and benzene. Insoluble in water.

Dehydration of 4-Phenylethinylheptan-4-ol with Acetic Anhydride

129 g of the alcohol was mixed with 280 ml acetic anhydride. The mixture was refluxed in a flask for 8 hours. The excess of acetic anhydride and the formed acetic acid were distilled off; three fractional distillations of the residual mass gave a light-yellow liquid with b.p. 110 - 112° (0.5 mm). Yield 98 g (82.6%); d_{20}^{20} 0.9049; n_D^{20} 1.5540.

0.1223 g substance: 0.4076 g CO_2; 0.1091 g H_2O. 0.1393 g substance: 0.4636 g CO_2; 0.1165 g H_2O. 0.2794 g substance; 23.26 g C_6H_6; Δt 0.32°. Found %: C 90.89, 90.77; H 9.91, 9.29; M 192.6. $C_{15}H_{18}$. Calculated %: C 90.86; H 9.14; M 198.1.

The prepared vinylacetylenic hydrocarbon – 4-phenylethinyl-3-heptene – had good solubility in the above-mentioned solvents, just like the alcohol. It did not exhibit any appreciable polymerization after standing for 7 months.

Oxidation of 4-Phenylethinyl-3-heptene with Acetyl Hydroperoxide

33.5 g of the vinylacetylenic hydrocarbon was oxidized in a medium of absolute ethyl ether at a temperature of +2° with 26 g of 69.1% acetyl hydroperoxide.

The reaction proceeded with insignificant rise of temperature to +4°. After addition to the hydrocarbon of the whole of the acetyl hydroperoxide, the mixture was allowed to stand at room temperature. The completion of the reaction was checked by withdrawing a 1 ml sample every 2 days, diluting it with water to 100 ml and titrating with 0.1 N thiosulfate. In this way it was established that the reaction of oxidation of 4-phenylethinyl-3-heptene with acetyl hydroperoxide took place over a period of 10 days, the concentration of hydroperoxide being found unchanged after further titration.

The nonreacted acetyl hydroperoxide and the formed acetic acid were removed by washing twice with water and once with 2% sodium carbonate solution. The ethereal layer containing the oxidation products was separated, dried with potassium carbonate for 24 hours and filtered. The ether was driven off and the residue fractionated in vacuum. Three fractionations gave the following:

1) b.p. 128 - 129° (0.5 mm), 1.8 g; 2) b.p. 156 - 159° (0.5 mm), 8 g; 3) b.p. 147 - 148° (2mm), 6.5 g.

Examination of substance with b.p. 128 - 129° (0.5 mm). This was a light-yellow liquid, soluble in ethyl ether, ethyl alcohol and chloroform; d_4^{20} 0.9743; n_D^{20} 1.5380.

0.1367 g substance: 0.4186 g CO_2; 0.1024 g H_2O. 0.1325 g substance: 0.4070 g CO_2; 0.0999 g H_2O. Found %: C 83.71, 83.77; H 8.32, 8.38. $C_{15}H_{18}O$. Calculated %: C 84.10; H 8.46.

The analytical data show that the substance is 4-phenylethinylheptene-3.

Examination of substance with b.p. 156 - 159° (0.5 mm). After fractional distillation it consisted of a viscous yellow liquid which crystallized on standing in the form of slender, white crystals with m.p. 108 - 109°.

0.1193 g substance: 0.3385 g CO_2; 0.0950 g H_2O. 0.1146 g substance: 0.3257 g CO_2; 0.0921 g H_2O. 0.1180 g substance: 25.70 ml CH_4 (18.5°, 733 mm). Found %: C 77.38, 77.51; H 8.85, 8.93; OH 15.02. $C_{15}H_{20}O_2$. Calculated %: C 77.55; H 8.66; OH 14.65.

The experimental data indicate that the substance is the acetylenic glycol, 4-phenylethinylheptane-3,4-diol which dissolves in ethyl ether, ethyl alcohol, methyl alcohol and chloroform and is insoluble in water.

The presence of a triple bond in the glycol was shown by quantitative bromination. 0,2029 g substance, dissolved in chloroform, added on 0,3050 g bromine, which is the theoretical amount for addition of four bromine atoms or 0,2797 g for one triple bond.

Examination of substance with b.p. 147-148° (2 mm). Yellow liquid, soluble in the same solvents as the acetylenic glycol.

d_4^{20} 1.0100; n_D^{20} 1.5312; MR_D 76.94; calculated 76.19.

0.1103 g substance: 0.3223 g CO_2; 0.0792 g H_2O. 0.1041 g substance: 0.3045 g CO_2; 0.0765 g H_2O. Found %: C 79.69, 79.77; H 7.98, 8.17. $C_{17}H_{20}O_2$. Calculated %: C 79.65; H 7.85.

The data show that the substance is the monoacetate of the vinylacetylenic hydrocarbon, 4-phenylethinyl-5-acetylhydroxy-3-heptene.

SUMMARY

1. The tertiary acetylenic alcohol, 4-phenylethinylheptan-4-ol, was synthesized and converted by acetic anhydride dehydration into the vinylacetylenic hydrocarbon, 4-phenylethinyl-3-heptene.

2. Oxidation of 4-phenylethinyl-3-heptene with acetyl hydroperoxide gave its oxide, also an acetylenic glycol — 4-phenylethinylheptane-3,4-diol — and a vinylacetylenic monoacetate — 4-phenylethinyl-5-acetylhydroxy-3-heptene; these are products of secondary reactions involving the oxide.

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* See Consultants Bureau Translation, p. a-151.

SULFONATION AND SULFONIC ACIDS OF ACIDOPHOBIC COMPOUNDS

XXIV. SULFONATION OF ISOBUTENE AND TRIMETHYLETHYLENE

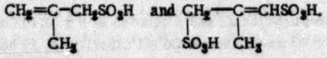
A. P. Terentyev, A. V. Dombrovsky and R. A. Gracheva

In 1947 A. P. Terentyev, in his paper on "Sulfonation and sulfonic acids of acidophobic compounds" [1] showed, on the basis of considerable experimental material, that pyridine-sulfotrioxide is a good sulfonating medium for substances which are easily modified by the action of acidic reagents. Sulfonation with this agent gives good yields of unsaturated sulfonic acids which possess well-marked activity at the double bond [2]. The activity of the double bond in isobutene and trimethylethylene is brought about by the positive inductive effect of the methyl groups which are unsymmetrically distributed at the double bond. Both these hydrocarbons possess great reactivity, and a large number of their chemical reactions have been studied including substitution of hydrogen atoms by various groups.

On treatment with sulfuric acid, isobutene and trimethylethylene undergo a whole series of complex transformations, mainly involving polymerization, hydration and resinification.

A. M. Butlerov [3] studied the polymerization of isobutene under the action of sulfuric acid. S. V. Lebedev and G. G. Koblyansky [4] later studied the polymerization of isobutene by Butlerov's method and obtained a complex mixture of products.

In 1941 Suter and co-workers [5] studied the action of dioxane-sulfotrioxide on isobutene. On passing the latter into a suspension of dioxane-sulfotrioxide in dichloroethane, they isolated a mixture of two sulfonic acids:

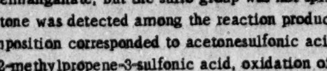


$$CH_2=\underset{CH_3}{\underset{|}{C}}-CH_2SO_3H \quad \text{and} \quad \underset{SO_3H}{\underset{|}{CH_2}}-\underset{CH_3}{\underset{|}{C}}=CHSO_3H.$$

Nothing about the sulfonation of trimethylethylene has appeared in the literature.

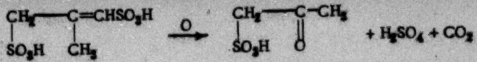
We attempted the sulfonation of isobutene and trimethylethylene under pressure, a mixture of a 50% solution of the hydrocarbons in dichloroethane and pyridine-sulfotrioxide being heated to 100-110°. The reaction mass was worked up to yield a mixture of the barium salts of the unsaturated sulfonic acids. It ought to be noted that the agent used in the reaction was the so-called "acid" pyridine-sulfotrioxide (containing 0.5% free sulfur trioxide). In both cases the mixture consisted of mono- and disulfonic acids.

2-Methylpropene-1 (isobutene). The yield of sulfonic acids was about 50%. Separation of the acids in the mixture was facilitated by the differing solubilities of their sodium salts in absolute ethyl alcohol. The structure of the obtained products was verified by oxidation. Rapid discoloration occurred when a salt of the monosulfonic acid was treated with potassium permanganate, but the sulfo group was not split off even after prolonged heating with the oxidizing agent. No acetone was detected among the reaction products. From the filtrate after oxidation was isolated a salt whose composition corresponded to acetonesulfonic acid. Consequently, the monosulfonic acid corresponded in structure to 2-methylpropene-3-sulfonic acid, oxidation of which proceeded according to the scheme:



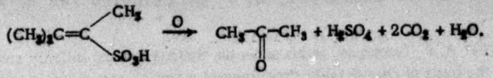
$$\underset{SO_3H}{\underset{|}{CH_2}}-\underset{CH_3}{\underset{|}{C}}=CH_2 \xrightarrow{O} CH_3-\underset{O}{\underset{\|}{C}}-CH_2SO_3H.$$

When permanganate reacts with the salt of the disulfonic acid, one-half of the sulfur is split off in the form of sulfate ion; it is clear that one sulfo group is located at the double bond. The salt of acetonesulfonic acid was found among the oxidation products. Consequently, the disulfonic acid has the structure of 2-methyl-propene-1, 3-disulfonic acid. Its oxidation proceeds according to the scheme:



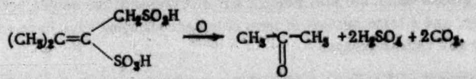
$$\underset{\displaystyle SO_3H}{CH_2}-\underset{\displaystyle CH_3}{C}=CHSO_3H \xrightarrow{O} \underset{\displaystyle SO_3H}{CH_2}-\underset{\displaystyle O}{\overset{\|}{C}}-CH_3 + H_2SO_4 + CO_2$$

2-Methylbutene-2 (trimethylethylene). Sulfonation of trimethylethylene gave a mixture of mono- and disulfonic acids in a total yield of 54.5%. The components were separated by reprecipitation of the saturated aqueous solutions of the barium salts with methyl alcohol. This treatment brings down the salt of the monosulfonic acid. Salts (K, Na, Ba) of the monosulfonic acid are quickly oxidized by permanganate solution, in which process the sulfo group is completely detached in the form of sulfate ion; acetone was detected among the reaction products. Consequently, the sulfonic acid had the structure of 2-methylbutene-2-sulfonic acid-3 whose oxidation proceeded according to the scheme:



$$(CH_3)_2C=C\begin{matrix}CH_3\\SO_3H\end{matrix} \xrightarrow{O} CH_3-\underset{\displaystyle O}{\overset{\|}{C}}-CH_3 + H_2SO_4 + 2CO_2 + H_2O.$$

Oxidation of the salt of the disulfonic acid in similar conditions showed that the whole of the sulfur is likewise split off in the form of sulfate ion; acetone was again found in the oxidation products. Consequently this acid corresponds to 2-methylbutene-2-disulfonic acid-3,4 which is decomposed as follows on oxidation:



$$(CH_3)_2C=C\begin{matrix}CH_2SO_3H\\SO_3H\end{matrix} \xrightarrow{O} CH_3-\underset{\displaystyle O}{\overset{\|}{C}}-CH_3 + 2H_2SO_4 + 2CO_2.$$

The free sulfonic acids, obtained by precipitation of the barium salts with sulfuric acid solution, are only stable in the form of solutions whose concentration does not exceed 75-80%. On further concentration they decompose with separation of sulfuric acid and resinous bodies.

EXPERIMENTAL

I. Sulfonation of 2-Methylpropene-1 (isobutene).

Isobutene was prepared by dehydration of isobutyl alcohol or by passing the latter over alumina at 300°. The gas was dried by passage over calcium chloride and was condensed in a receiver immersed in a freezing mixture.

46 g (0.284 mole) pyridine-sulfotrioxide and a solution of 8 g (0.142 mole) isobutene in 12.6 ml dichloroethane were heated in a stainless steel autoclave of 500 ml capacity for 10 hours at 100-110°. When the autoclave was opened the unreacted isobutene escaped; there was no sulfur dioxide. The sulfonation product, a viscous mass, deliquescing in the air, was dissolved in water and treated with concentrated ammonia. The aqueous-ammoniacal layer was separated and washed several times with benzene to remove the pyridine; it was then treated with excess of barytes and evaporated to dryness. The dry residue was dissolved in water; the excess of barytes was precipitated with carbon dioxide. The filtrate, containing the barium salts of the sulfonic acids, was evaporated on a water bath. Water was removed from the salt by boiling with benzene. Yield 18 g white crystalline salt whose aqueous solutions were decolorized by bromine water and potassium permanganate.

5.707 mg substance: 3.425 mg $BaSO_4$. 3.714 mg substance: 2.257 mg $BaSO_4$. Found %: Ba 35.31, 35.76. $(C_4H_7O_3S)_2Ba$. Calculated %: Ba 33.69. $C_4H_6O_6S_2Ba$. Calculated %: Ba 39.07

The analysis shows that a mixture of mono- and disulfonic acids was obtained. For the purpose of separating these, their barium salts were converted into sodium salts by addition of the equivalent amount of sodium sulfate. The filtrate was evaporated to dryness and the salt dried by boiling with benzene. 10 g of the obtained sodium salt was placed in an extractor for extraction with boiling alcohol. Extraction with 150 ml hot absolute alcohol for 32 hours yielded 3.1 g sodium salt whose composition corresponded to the monosulfonic acid.

3.893 mg substance: 1.720 mg Na_2SO_4. Found %: Na 14.64. $C_4H_7O_3SNa$. Calculated %: Na 14.54.

The insoluble portion contained 6.5 g salt whose sodium content corresponded to the disulfonic acid.

5.770 mg substance: 3.055 mg Na_2SO_4. Found %: Na 17.14. $C_4H_6O_6S_2Na_2$. Calculated %: Na 17.68.

Oxidation of the sodium salt of the monosulfonic acid. To 1.5 g salt in 30 ml water was added in small portions with frequent shaking, 3 g finely pulverized potassium permanganate. After 4 hours' heating decolorization had taken place. The filtrate was evaporated to a small volume and worked up with barium chloride solution. The resultant white precipitate, after treatment with dilute acetic acid solution, was dissolved in hot water and the filtrate was evaporated. The resultant crystals of barium salt were recrystallized from hot water. The analysis corresponded to acetonesulfonic acid.

8.778 mg substance: 4.986 mg $BaSO_4$. Found %: Ba 33.42. $(C_3H_5O_4S)_2Ba$. Calculated %: Ba 33.43.

Oxidation of the sodium salt of the disulfonic acid. 2.5 g salt was oxidized with 5 g potassium permanganate. The filtrate was treated with barium chloride. The precipitate of barium sulfate weighed 2.29 g which corresponded to cleavage of one sulfo group. The filtrate also contained the barium salt of acetonesulfonic acid.

II. Sulfonation of 2-Methylbutene-2 (Trimethylethylene)

Trimethylethylene was prepared by the N. D. Zelinsky reaction by the procedure described by S. G. Krapivin [6] (heating of isoamyl alcohol with anhydrous oxalic acid). Constants of the prepared hydrocarbon: b.p. 35.5°, d_4^{17} 0.6647, n_D^{17} 1.3888, in accord with the literature.

7 g (0.1 mole) trimethylethylene in 10.5 ml dichloroethane was sulfonated with 32 g (0.2 mole) pyridine-sulfotrioxide by the same procedure as for isobutene. Working up in the appropriate manner led to isolation of 21.5 g barium salts.

6.261 mg substance: 3.765 mg $BaSO_4$. Found %: Ba 35.34. $(C_5H_9O_3S)_2Ba$. Calculated %: Ba 31.52. $C_5H_8O_6S_2Ba$. Calculated %: Ba 37.57.

Separation of the individual salts. A saturated aqueous solution of 10 g barium salt was precipiated with methyl alcohol. The salt of the monosulfonic acid came down. After 3 reprecipitations, two salt fractions were isolated: 1) 4 g, corresponding to the monosulfonic acid, and 2) 6 g, corresponding to disulfonic acid.

Barium determination in the salt of the monosulfonic acid:

10 mg substance: 5.413 mg $BaSO_4$. Found %: Ba 31.53. $(C_5H_9O_3S)_2Ba$. Calculated %: Ba 31.52.

Barium determination in the salt of the disulfonic acid:

8.085 mg substance: 5.194 mg $BaSO_4$. Found %: Ba 37.80. $C_5H_8O_6S_2Ba$. Calculated %: Ba 37.57.

Oxidation of the salt of the monosulfonic acid. 2 g salt in 20 ml water was oxidized by addition of 5.5 g finely pulverized potassium permanganate. At the conclusion of the reaction, a few milliliters was distilled off and tested for acetone by adding alkali followed by iodine in potassium iodide; the characteristic crystals of iodoform were precipitated. Barium ions were not detected in the filtrate. Barium sulfate was isolated from the precipitate, after dissolution of the manganese dioxide.

Oxidation of the barium salt of the disulfonic acid. 2 g barium salt of the disulfonic acid was oxidized in the same conditions as in the preceding case. Barium sulfate was found in the precipitate after working up with hydrochloric acid. The filtrate was treated with barium chloride to give 1.2 g barium sulfate, which corresponds to the second sulfo group. In the filtrate, after oxidation, acetone was detected by the iodoform reaction.

SUMMARY

1. Pyridine-sulfotrioxide was used for sulfonation of isobutene and trimethylethylene. In both cases a mixture of mono- and disulfonic acids was obtained.

2. Resolution of the mixture of sulfonic acids was accomplished by fractional crystallization of their salts. The structure of the acids was demonstrated by oxidation with $KMnO_4$.

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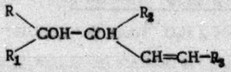
SYNTHESIS AND TRANSFORMATION OF α-GLYCOLS OF THE OLEFINIC SERIES

I. PREPARATION OF 2-METHYL-3,5-DIPHENYLPENTENE-4-DIOL-2,3

L. F. Chelpanova and Z. V. Printseva

In spite of the numerous investigations in the field of glycols of the olefinic series, the synthesis and transformation of disecondary olefinic α-glycols (pinacones) of the type of (I) have hardly been studied.



(I)

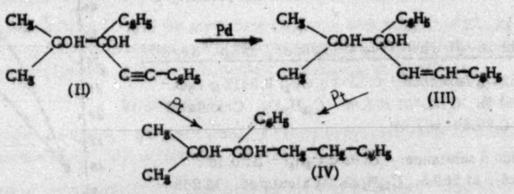
We set out to investigate the transformations of this type of compound in the presence of acid catalysts, selecting in the first instance 2-methyl-3,5-diphenylpentene-4-diol-2,3 (III) as the object of study.

In this paper we describe the synthesis and properties of this substance.

For the preparation of 2-methyl-3,5-diphenylpentene-4-diol-2,3 we employed the method of catalytic hydrogenation of the corresponding acetylenic α-glycol—dimethylphenyl-phenylethinyl-ethylene glycol (2-methyl-3,5-diphenylpentyne-4-diol-2,3) (II) [1]. Pinacones of this type, as shown by E. D. Venus-Danilova and co-workers [2-8], can be readily synthesized by the Zh. I. Iotsich method.

Following the addition of 2 atoms of hydrogen in presence of colloidal platinum, 2 geometrical isomers were isolated: the cis-isomer with m.p. 56-57° and the transisomer with m.p. 86-87°. Further hydrogenation of both isomers with platinum black gives one and the same saturated glycol, although the cis-isomer adds on hydrogen twice as quickly as the trans-isomer.

The same saturated glycol —2-methyl-3,5-diphenylpentane-diol-2,3 (IV) —was obtained by reduction of the original acetylenic glycol in presence of platinum black.



EXPERIMENTAL

Synthesis of 2-Methyl-3,5-diphenylpentene-4-diol-2,3

The α-glycol was synthesized by the method of catalytic hydrogenation of the acetylenic glycol in the presence of colloidal palladium. The colloidal palladium was prepared on gum arabic by Loew's method [9]

Hydrogenation was carried out in an ordinary hydrogenation flask with mechanical shaking. Hydrogen was charged into the reaction flask in quantity necessary for conversion of the triple bond into a double bond. One of the experiments is detailed in Table 1.

From the data of Table 1 we see that hydrogen absorption proceeds smoothly. After separating the catalyst and dis[illegible]g off the solvent, colorless crystals were obtained which were washed on the filter with cold ligroin.

The ligroin -insoluble substance melted at 86-87°. After driving off the ligroin and repeated crystallizations, a substance with m.p. 56-57° was isolated from the mother liquor. The melting points of both substances did not change after recrystallization from hot ligroine. Both substances decolorize bromine water and aqueous potassium permanganate. The molecular data show that the two compounds have the same composition and molecular weight. Hydrogenation of both substances in presence of platinum black gives one and the same saturated glycol with m.p. 72-73°.

TABLE 1

2.66 -moles acetylenic glycol; 50 ml alcohol; 5 mg Pd (6 ml Pd). Pressure 759 mm, temp. 20°, calculated H_2,242 ml

T.	5	10	15	20	25	30	35	40	45
v.	38	78	110	133	156	178	200	222	242
% H_2. . . .	15.7	32.2	54.4	54.9	64.4	73.1	82.6	91.7	100

T is the time in minutes from the start of the experiment; v is the volume of hydrogen absorbed from the start of the experiment; % H_2 is the volume of hydrogen in percentages.

On the basis of these data we may conclude that the crystals with m.p. 56-57° and 86-87° are geometrical isomers and that, apparently, the one with m.p. 56-57° is the cis-isomer and the other the trans-isomer.

Examination of the Trans-Isomer with m.p. 56-57°.

0.0758 g substance: 0.2212 g CO_2; 0.0500 g H_2O. Found %: C 81.10; H 7.38. $C_{18}H_{20}O_2$. Calculated %: C 80.60; H 7.83.

0.0934 g substance; 11.00 g C_6H_6: Δt 0.16°. Found: M 265.9. $C_{18}H_{20}O_2$. Calculated: M 268.

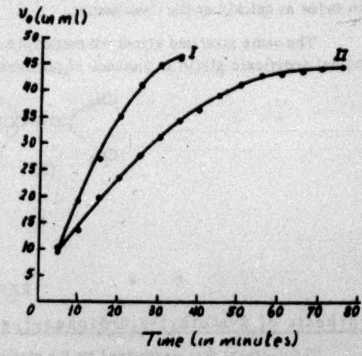
0.0232 g substance: 4.4 ml CH_4 (15°, 757 mm). Found: v_0 4.0 ml; % OH 13.23. $C_{18}H_{18}(OH)_2$. Calculated: v_0 3.86 ml, % OH 12.75.

The compound is readily soluble in common solvents: with strong sulfuric acid it gives a bright-red coloration with a marked greenish fluorescence which disappears on dilution with water.

Addition of two atoms of hydrogen to the cis-isomer proceeds fairly quickly, as is evident from the diagram (curve I—cis-isomer).

Hydrogenation was carried out with 0.5 g glycol, 0.3 g platinum black and 25 ml alcohol; pressure 758 mm, temp. 16°. Theoretical amount of hydrogen 45 ml.

After separating the catalyst and distilling off the solvent, colorless crystals with m.p. 72-73° were obtained which did not decolorize bromine water and potassium permanganate;



Examination of the Trans-Isomer, m.p. 86-87°

0.0524 g substance: 0.1571 g CO_2; 0.0412 g H_2O. Found %: C 81.75; H 8.80. $C_{18}H_{20}O_2$. Calculated %: C 80.60; H 7.83.

0.0950 g substance: 11.02 g C_6H_6: Δt 0.16°. Found: M 269.5. $C_{18}H_{20}O_2$. Calculated: M 268.

0.048 g substance: 8.5 ml CH_4 (15°, 757 mm). Found: v_0 8.2 ml; % OH 13.00. $C_{18}H_{20}(OH)_2$. Calculated: v_0 8.0 ml; % OH 12.69.

The substance is sparingly soluble in cold ligroin: it dissolves in ordinary organic solvents. With strong sulfuric acid it slowly gives a dark-red coloration which persists for a long period. On dilution with water the color disappears.

Addition of two atoms of hydrogen led to isolation of crystals with m.p. 72-73°, which did not give a melting point depression with the substance obtained by hydrogenation of the cis-isomer. The trans-isomer adds on hydrogen twice as slowly as the cis-isomer, as shown in the diagram (curve II—trans-isomer).

The quantities of reagents and the conditions for hydrogenation of the trans-isomer were similar to those for the cis-isomer.

Preparation of 2-Methyl-3,5-diphenyl-pentanediol-2,3

The saturated glycol was prepared by hydrogenation of the acetylenic glycol both in presence of colloidal palladium and in presence of platinum black. Results are set forth in Tables 2 and 3.

Hydrogen adds on smoothly to the acetylenic glycol to form the saturated glycol; no halt in the velocity of hydrogenation was observed after addition of 2 atoms of hydrogen, such as had been observed for γ-acetylenic glycols [10]; a crystalline substance with m.p. 72-73° was isolated in both cases after addition of 4 atoms of hydrogen.

TABLE 2

2.56 g (0.01 mole) acetylenic pinacone; 50 ml ethyl alcohol; 6 mg Pd (6 ml Pd). Pressure 755 mm, temp. 20°, calculated $2H_2$, 488.2 ml

T. . .	3	6	9	12	15	18	21	24	27	30	33	36	40
v . . .	108	192	256	309	352	386	413	437	457	473	481	487	490

TABLE 3

1.33 g (0.0051 mole) acetylenic glycol; 50 ml alcohol; 0.4 g platinum black. Pressure 779.5 mm, temp. 16°, calculated $2H_2$, 234 ml

T. . .	10	20	30	40	50	60	70	80	90	100	110	120	130
v . . .	50	85	113	137	159	177	193	207	217	224	228	232	234

Investigation of the Saturated Glycol with m.p. 72-73°.

0.1029 g substance; 0.3025 g CO_2; 0.0760 g H_2O. Found %: C 80.40; H 8.30; $C_{18}H_{22}O_2$. Calculated %: C 80.00; H 8.10.

0.2096 g substance; 12.36 g C_6H_6; Δt 0.31°. Found: M 273.5. Calculated: M 270.0.

0.0252 g substance: 4.5 ml CH_4 (15°, 755.5 mm). Found: v_0 4.2 ml; %OH 12.68. $C_{18}H_{20}(OH)_2$. Calculated v_0 1.18 ml; % OH 12.59.

The glycol with m.p. 72-73° (from ligroin) did not decolorize bromine water and aqueous potassium permanganate; in presence of strong sulfuric acid it carbonizes; it dissolves in the common organic solvents.

Oxidation of the saturated glycol with manganese triacetate [11]. To a flask containing 6.5 g manganese triacetate and 100 ml glacial acetic acid was added a solution of 5 g of the saturated glycol (m.p. 72-73°) in 100 ml glacial acetic acid over a period of 5 hours at 80-85° with constant stirring. After completion of the reaction, the solution had acquired a lemon-yellow color. On cooling, a precipitate of manganese diacetate came down and was filtered off. The filtrate was neutralized and distilled with steam; the distillate was extracted with ether; acetone was detected in the aqueous residue from the distillate; after salting-out, it was distilled into a solution of 2,4-dinitrophenylhydrazine. The resultant acetone 2,4-dinitrophenylhydrazone had m.p. 125-126° and did not give a melting point depression with authentic acetone 2,4-dinitrophenylhydrazone.

From the ethereal extract was isolated 0.7 g of the crystalline substance with m.p. 71-72°. Its oxime had m.p. 82-83°. These melting points correspond to those of 1,3-diphenylpropanone-1, which has been described in the literature [12]. The dinitrophenylhydrazone of this ketone (yellow needles) had m.p. 142-144°.

SUMMARY

1. 2-Methyl-3,5-diphenylpentene-4-diol-2,3 was synthesized by catalytic hydrogenation of 2-methyl-3,5-diphenylpentyne-4-diol-2,3 in presence of colloidal palladium.

2. Two geometrical isomers of the olefinic glycol were isolated and characterized: m.p. 56-57° and 86-87° (cis- and trans-isomers).

3. It was shown that a saturated glycol with m.p. 72-73° is obtained by reduction of the cis- and trans-isomers of the olefinic glycol with platinum black as well as by reduction of the acetylenic glycol both with platinum black and colloidal palladium.

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SYNTHESIS AND TRANSFORMATIONS OF ACETYLENIC ALCOHOLS CONTAINING POLYMETHYLENE RINGS

I. 1-PHENYLETHINYL-CYCLOPENTANOL-1

E. D. Venus-Danilova and M. V. Gorelik

Hydration of tertiary acetylenic alcohols of the type of $RR_1C(OH){-}C{\equiv}CH$ usually leads to tertiary α-keto-alcohols with an acetyl group: $RR_1C(OH){-}COCH_3$ [1].

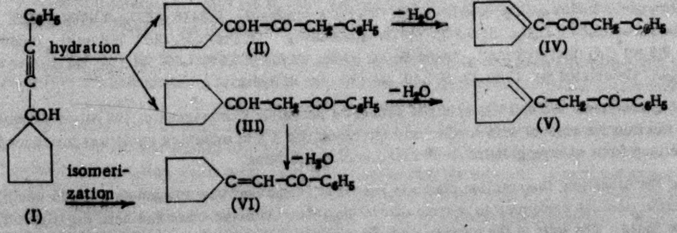
Hydration of tertiary alcohols containing a vinylacetylenic residue has been studied by I.N. Nazarov and co-workers [2, 3]. In this case, in presence of mercuric sulfate and sulfuric acid, the alcohols isomerize to form substituted divinyl ketones and products of their further transformation — substituted tetrahydrofurans.

We have investigated the hydration of tertiary alcohols containing substituted acetylenic residues as well as polymethylene rings by the method of M.G. Kucherov under Scheibler's conditions [4].

As the first object for investigation we selected 1-phenylethinyl-cyclopentanol-1 (I), an interesting compound in that, according to the data of I.N. Nazarov, such a tertiary vinylacetylenic alcohol with a pentamethylene ring forms a divinyl ketone in very low yield by treatment with mercuric sulfate in mild conditions in acetone solution, whereas at a higher temperature the alcohol is dehydrated with considerable resinification [3].

1-Phenylethinyl-cyclopentanol-1 (I), not previously known, was synthesized by Zh. I. Iotsich's method. The structure of the alcohol was established by analyses and from the composition of the products of its oxidation (benzoic and hydroxycyclopentane carboxylic acids).

On hydration of the acetylenic alcohol (I) the formation is possible of α (II) and β (III) ketoalcohols, while their dehydration could lead to the unsaturated ketones (IV), (V) and (VI); in the event, however, of isomerization of 1-phenylethinyl-cyclopentanol-1 (I), another possibility is formation of an unsaturated ketone (VI) — cyclopentylidene-acetophenone.



Investigation of the products obtained by the action of mercuric sulfate and sulfuric acid on 1-phenylethinyl-cyclopentanol-1 (I) showed that the sole product of this reaction is the unsaturated ketone, cyclopentylidene-acetophenone (VI), whose structure was established by oxidation with potassium permanganate (cylcopentanone, glutaric acid and benzoic acid were isolated), by ozonolysis (cyclopentanone and benzoic acid were isolated) and by the preparation of the corresponding pyrazoline.

α-Δ'-Cyclopentenyl-acetophenone (V) has been described in the literature [5]; the constants and properties of this ketone do not agree with those of the unsaturated ketone that we prepared. It has also been reported that condensation of cyclopentanone with acetophenone does not give an olefinic ketone (neither V nor VI). Formation of cyclopentylidene-acetophenone (VI) could result from hydration of the original acetylenic alcohol to a β-ketoalcohol (III) with further dehydration of the latter; another possibility is the direct isomerization of 1-phenylethinylcyclopentanol.

The β-ketoalcohol (III) is bound to possess very labile hydrogen atoms in the methylene group and is easily dehydrated with formation of cyclopentylideneacetophenone; consequently, it cannot be detected in the reaction products.

The second hypothesis is also probable, bearing in mind the increased lability of the hydroxyl group standing in the α-position to the triple bond, as confirmed by the numerous investigations of many chemists [6]. This lability of the hydroxyl group and the susceptibility of the acetylenic alcohol to the acetylene-allene rearrangement is intensified by the presence of the phenyl group and by the acid catalyst.

Experiments with use of a more dilute solution of mercuric sulfate and a lower content of free sulfuric acid, also experiments with sulfuric acid alone, enable clarification of the course of the transformation of 1-phenylethinylcyclopentanol-1 into cyclopentylidene-acetophenone.

EXPERIMENTAL

1-Phenylethinyl-cyclopentanol-1 (I)

Synthesis. We describe one of the experiments on preparation of 1-phenylethinyl-cyclopentanol-1 starting from 12 g magnesium, 64 g ethyl bromide, 51 g phenylacetylene and 42 g cyclopentanone. Preparation of the phenylethinylmagnesium bromide proceeded normally with evolution of the theoretical amount of ethane. The ethereal solution of cyclopentanone was run in slowly, with stirring and cooling to 0°. The obtained complex was decomposed carefully with 8% sulfuric acid; the ether extract was washed with dilute aqueous sodium carbonate solution and dried with sodium sulfate. The ether was driven off to leave a viscous, dark liquid (90 g) which did not crystallize on standing. The residue of unreacted phenylacetylene was distilled off in vacuum (b.p. 49-51° at 25 mm); after this, however, the substance did not crystallize and set to a yellow-brown mass. At 1 mm pressure the substance boiled at 113-118° with partial decomposition, forming a semisolid mass which did not give definite crystals.

The residue after removal of the phenylacetylene was purified by dissolving it in a small amount of ethyl alcohol (or methyl alcohol) and diluting the solution with 20-25 times the amount of cold water. An emulsion was formed which, after a day, deposited long, slender crystals resembling glass wool. In the dry condition they resembled felt and had m.p. 41-42°. In this method of purification, all the resinous impurities either floated to the surface to form a solid film or sank to the bottom. By repeated solution and precipitation with water of the impurities it was possible to isolate an additional considerable amount of the pure substance. The procedure results in considerable losses of material (yield 30-35% of the theoretical), but the product is obtained in a very pure form, especially if dissolution and reprecipitation are performed twice.

0.1505 g substance: 0.4509 g CO_2; 0.1054 g H_2O. 0.1114 g substance: 0.3416 g CO_2; 0.0762 g H_2O. 0.1686 g substance; 12.54 g C_6H_6: Δt 0.36°. 0.0763 g substance: 11.7 ml CH_4 (20°, 769 mm). 0.0606 g substance: 9.0 ml CH_4 (20°, 768 mm). Found %: C 83.52, 83.61; H 7.78, 7.60. M 190. No. hydroxyl groups 1.17. $C_{13}H_{14}O$. Calculated %: C 83.87; H 7.53. M 186. No. of hydroxyl groups 1.

Oxidation. 5 g acetylenic alcohol was oxidized with 8.4 g potassium permanganate; 400 ml of 1% permanganate solution was run into the alcohol with stirring, and the remaining 4 g of oxidizing agent was introduced in the dry, finely pulverized form with progressive decolorization of the solution.

At the end of the oxidation, the reaction mass was heated to 50-55° and the manganese dioxide was filtered off; an ether extraction was performed to remove neutral products. After the ether had been distilled off, no neutral products were found. The salts of the organic acids were inspissated and decomposed with dilute sulfuric acid, and the precipitated solid acids (3.5 g) were filtered off. M.p. 113°. A portion of these acids was converted into the silver salts by heating with freshly precipitated silver carbonate; the silver contents were determined in the silver salts after fractional recrystallization.

First fraction 0.0803 g salt: 0.0378 g Ag; % Ag 47.07; 0.1001 g salt: 0.0472 g Ag; % Ag 47.15 Fraction 4 0.0913 g salt: 0.0418 g Ag; % Ag 45.78; 0.1082 g salt: 0.0495 g Ag; % Ag 45.84. $C_7H_5O_2Ag$. Calculated %: Ag 47.16. $C_6H_9O_3Ag$. Calculated %: Ag 45.57.

Analysis of the silver salts shows that oxidation gave a mixture of benzoic and hydroxycyclopentane carboxylic acids.

Pure benzoic acid with m.p. 120-121° was isolated from the mixture by sublimation and its structure was confirmed by a mixed melting test with an authentic specimen.

After the solid acids had been removed, ether extraction of the solution yielded a light-yellow, viscous substance which crystallized on standing. After purification, it melted at 102-103°. The acid was converted into a silver salt whose analysis corresponded to the silver salt of α-hydroxycyclopentane carboxylic acid.

0.1100 g substance: 0.1211 g CO_2; 0.0442 g H_2O; 0.0504 g Ag. Found %: C 30.02; H 4.46; Ag 45.82. $C_6H_9O_3Ag$. Calculated %: C 30.38; H 4.22; Ag 45.57.

Transformation of 1-Phenylethinyl-cyclopentanol-1

16 g 1-phenylethinyl-cyclopentanol-1 and 60 ml of a solution of mercuric sulfate, in sulfuric acid [prepared from 5 g HgO, 25 ml H_2SO_4(sp.gr. 1.84) and 150 ml H_2O] [7] was heated for 3 hours at 60-70°. Ether extraction was carried out, the extract was washed with dilute sodium carbonate and water, and dried with sodium sulfate. The residue, after removal of the ether, weighed 16.1 g and after two distillations (7 mm) gave the following fractions:

1) b.p. 145-147°; n_D^{18} 1.585 – 1.1 g; 2) b.p. 147-150°; n_D^{18} 1.582 – 2.0 g; 3) b.p. 150-151°; n_D^{18} 1.580 – 5.8 g; 4) b.p. 151-152.5°; n_D^{18} 1.580 – 5.2 g; in the residue after fractionation – 1.1 g resins.

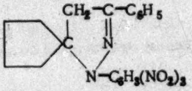
The third and fourth fractions were combined and subjected to investigation.

0.2404 g substance: 0.7312 g CO_2; 0.1666 g H_2O. 0.1201 g substance: 0.3681 g CO_2; 0.0838 g H_2O. 0.2286 g substance; 16.21 g C_6H_6: Δt 0.39°. Found %: C 83.52, 83.59; H 7.70, 7.76. M 184.6. $C_{13}H_{14}O$. Calculated %: C 83.87; H 7.53. M 186.

d_0^0 1.0625; d_{20}^{20} 1.0483; d_4^{20} 1.0465; n_D^{18} 1.580. Found MR_D 58.7. $C_{13}H_{14}O$. Calculated MR_D 56.0.

The substance did not give off a gas when reacted with methylmagnesium iodide; it instantaneously decolorized an aqueous solution of potassium permanganate and a solution of bromine in chloroform. With semicarbazide in aqueous alcoholic solution it slowly forms an uncharacteristic precipitate with an indefinite melting point (193-213°) which could not be readily purified.

With 2,4-dinitrophenylhydrazine, there is at once formed an orange-red, finely crystalline precipitate which, after crystallization from boiling ethyl alcohol melts at 157-158°, gives pyrazoline reactions, and has an analysis corresponding to



0.0873 g substance: 11.7 ml N_2 (15°, 752 mm). 0.0924 g substance: 12.6 ml N_2 (18°, 733 mm). Found %: N 15.68, 15.43. $C_{19}H_{18}O_4N_4$. Calculated %: N 15.33.

Oxidation. To 3 g substance with b.p. 150-152.5° (7 mm) was gradually added 320 ml 1% aqueous solution of potassium permanganate. The reaction is very energetic, decolorization being instantaneous; 2 g of the oxidant was introduced gradually in the dry form. After introduction of the theoretical amount of potassium permanganate (5.2 g), the oxidation was taken still further by addition of a fresh quantity of permanganate. The manganese dioxide was filtered off and washed with a little water. The filtrate was subjected to boiling to drive off volatile, neutral products of oxidation which were collected in semicarbazide solution. A semicarbazone came down immediately; it weighed 0.81 g in the dry state and melted at 204° after recrystallization. A lowering of the melting point was not observed in admixture with an authentic specimen of cyclopentanone semicarbazone. Yield of cyclopentanone (converted from the semicarbazone) 36% of the theoretical.

The salts of the organic acids were concentrated and decomposed with dilute sulfuric acid. A voluminous precipitate came down and was identified as benzoic acid by the usual tests. The filtrate after removal of the benzoic acid, was extracted with ether; the ether was driven off from the extract to leave an acid with m.p. 95-96°, which was converted to the silver salt. The latter was fractionally crystallized. Analysis of the third fraction of silver salts corresponded to the salt of glutaric acid; the first fraction was contaminated with silver benzoate.

First fraction 0.1303 g salt: 0.0758 g Ag; % Ag 58.17. Third fraction 0.1293 g salt: 0.0801 g Ag; % Ag 62.20. $C_5H_6O_4Ag_2$. Calculated %: Ag 62.43. $C_7H_5O_2Ag$. Calculated %: Ag 47.16.

The absence of benzoylformic acid from the oxidation products and the presence of a small quantity of cyclopentanone are evidence that oxidation of the initial products of oxidation — benzoylformic acid and cyclopentanone — continued to benzoic and glutaric acids.

Ozonolysis was performed in chloroform followed by isolation of the neutral and acidic products as in the preceding experiment. Ozonolysis of 3 g substance gave 1.5 g cyclopentanone semicarbazone (not recrystallized), corresponding to 0.91 g cyclopentanone (66 % of the theoretical).

From the acids obtained by acidification of the salts was isolated only 1.4 g unpurified benzoic acid (73.7%). Although the aqueous solution of the acids gave a weak qualitative reaction for benzoylformic acid (yellow flocculent precipitate with aqueous phenylhydrazine hydrochloride [8]), we failed to isolate it in the pure form or in the form of silver salt, due to its negligible amount.

The products of ozonolysis of the unsaturated ketone — cyclopentanone and benzoic acid[*] (product of decomposition of benzoylformic acid) — confirm the structure of cyclopentylidene-acetophenone.

SUMMARY

1. 1-Phenylethinyl-cyclopentanol-1 was synthesized by Zh. I. Iotsich's method.

2. It was shown that under the conditions of M.G.Kucherov's reaction, 1-phenylethinylcyclopentanol-1 is transformed into cyclopentylidene-acetophenone.

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[*] Evidently the benzoylformic acid decomposed during decomposition and heating of the ozonides.

[**] See Consultants Bureau Translation, page 159.

[***] " " " " " a-197.

[****] " " " " " 87.

[*****] " " " " " 1997, 2477.

SYNTHESIS AND PROPERTIES OF ETHERS OF DISECONDARY γ-GLYCOLS

III. PREPARATION OF BUTYL AND ISOAMYL ETHERS OF DIPHENYLBUTYNEDIOL, DIPHENYLBUTENEDIOL AND DIPHENYLBUTANEDIOL

Yu. S. Zalkind,* E. D. Venus-Danilova and V. N. Mikhailova

We have previously [1] described the synthesis of the full methyl, ethyl, propyl and isopropyl ethers of diphenylbutynediol, diphenylbutenediol and diphenylbutanediol.

In this paper we describe the preparation of the full butyl (Ia) and isoamyl (Ib) ethers of diphenylbutynediol and their hydrogenation to the corresponding ethers of the olefinic series (IIa and b) and of the saturated series (IIIb) by the procedure described in the previous communication [1].

$$\underset{\text{(Ia and b)}}{C_6H_5-CH(OR)-C\equiv C-CH(OR)-C_6H_5} \xrightarrow[Pd]{H_2} \underset{\text{(IIa and b)}}{C_6H_5-CH(OR)-CH=CH-CH(OR)-C_6H_5} \xrightarrow[Pt]{H_2}$$

$$\longrightarrow \underset{\text{(IIIb)}}{C_6H_5-CH(OR)-CH_2-CH_2-CH(OR)-C_6H_5}$$

Ia R = C_4H_9; Ib R = C_5H_{11} iso; IIa R = C_4H_9; IIb R = C_5H_{11} iso;
IIIb R = C_5H_{11} iso.

EXPERIMENTAL

I. Synthesis of Butyl and Isoamyl Ethers of Diphenylbutynediol (Ia and b)

These ethers were synthesized by Mamedov's method [2] from diphenylbutynediol with m.p. 140-142° prepared by Iotsich's method [3].

The results of experiments on the preparation of the butyl and isoamyl ethers of diphenylbutynediol are set forth in Table 1.

TABLE 1

Expt. No.	Amount				Duration of reaction (in hours)	Temp. (in °)		Yield of ether	
	of diphenylbutynediol (in g)	C_4H_9OH (in ml)	$C_5H_{11}OH$-iso (in ml)	H_2SO_4 (sp. gr. 1.83) (in ml)		of expt.	of boiling of the corresponding ether	(in g)	(in %)
1	5	50	–	2	6	80-90	200-207 (3mm)	2.45	16.60
2	5	50	–	2	7	80-90	200-207 (3mm)	2.45	16.60
3	7	50	–	2.5	24	80-90	200-205 (3mm)	5.7	38.77
4	10	50	–	2.5	19	80-90	200 (3mm)	5.1	34.70
5	10	50	–	2.5	21	80-90	200-205 (3mm)	6.5	44.21
6	10	50	–	2.5	24	80-90	200-207 (3mm)	6.0	40.81
7	10	–	50	2.5	24	80-90	210-215 (3mm)	5.4	34.00
8	10	–	50	2.5	17	80-85	205-215 (3mm)	4.8	32.26
9	10	–	50	2.5	24	80-85	210-215 (3mm)	5.0	31.48

The obtained ethers of diphenylbutynediol react with methylmagnesium iodide, which indicates the presence of a mixture of full and partial ethers of diphenylbutynediol. For the purpose of isolating the full ethers of diphenylbutynediol, chemical purification was effected by our previously described method [1]. It must be pointed out, however, that on treating the mixture of ethers of diphenylbutynediol with ethylmagnesium bromide, the formed organomagnesium complex dissolves in the ether ether; the reaction must consequently be carried out in a medium of dry benzene.

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* Deceased.

TABLE 2

Properties of Ethers of Diphenylbutyne-, Diphenylbutene- and Diphenylbutanediols

Formula of ether	Boiling point	d_{20}^{20}	n_D^{20}	Mol. wt.		MR$_D$		% C		% H	
				found	cal.	found	calc'd	found	calc'd.	found	calc'd
Ia $C_{24}H_{30}O_2$	202-204 (3mm)	1.0018	1.5333	362	350	107.23	107.11	82.10	82.28	8.63	8.57
Ib $C_{26}H_{34}O_2$	212-214 (3mm)	0.9924	1.5269	380.6	378	117.08	116.35	82.34	82.54	9.11	8.99
IIa $C_{24}H_{32}O_2$	175-180 (2mm)	0.9910	1.5233	348.9	352	107.23	107.15	81.75	81.82	9.28	9.09
IIb $C_{26}H_{36}O_2$	180-182 (2mm)	0.9880	1.5300	377.1	380	118.73	117.92	81.95	82.10	9.60	9.47
IIIb $C_{26}H_{38}O_2$	158-158 (3mm)	0.9860	1.5252	378.0	382	118.76	118.39	81.50	81.67	10.10	9.94

The purification led to isolation of the full butyl and isoamyl ethers of diphenylbutynediol.

The properties of the prepared ethers of diphenylbutynediol are set forth in Table 2.

The partial ethers of the glycol in question were not subjected to investigation due to their insignificant amounts.

Hydrolysis of the full butyl ether and the full isoamyl ether of diphenylbutynediol. Hydrolysis was performed with 2 g of the butyl ether of diphenylbutynediol (b.p. 202-204° at 3 mm) and 50 ml 7% sulfuric acid. The reaction was effected by heating to 70-85° with continuous stirring for 10 hours. At the end of the reaction, neutralization was performed with sodium carbonate solution and the reaction products were extracted with ether. After drying and driving off the ether, a nearly colorless liquid was obtained from which crystals came down after a short interval. These melted at 140° after recrystallization from aqueous alcohol and did not give a melting point depression with pure diphenylbutynediol.

Consequently, the formation of diphenylbutynediol on hydrolysis confirms the structure of the original ether.

II. Bromination of the Butyl (Ia) and Isoamyl (Ib) Ethers of Diphenylbutynediol

To a solution of 1 g of the full butyl ether of diphenylbutynediol in 15 ml dry chloroform was added dropwise with continuous stirring 9 ml of a 10% solution of bromine in chloroform (amount calculated for 4 atoms of bromine per molecule of initial ether). After 8 hours' heating at 40° with constant stirring and 12 hours' standing, the reaction mixture retains its dark-yellow color. Evolution of hydrogen bromide during the reaction period was not observed.

The nonreacted bromine was removed by washing with sodium carbonate solution and water. After the reaction mixture had been dried, the ether was driven off, leaving in the distillation flask a fairly viscous liquid (weight 0.85 g) which decomposed when fractionated in vacuum. For this reason the products of bromination were analyzed immediately after removal of the excess of bromine and distillation of the solvent.

0.1824 g substance: 0.1310 g AgBr. 0.1646 g substance: 0.1191 g AgBr. Found %: Br 30.55, 30.78. $C_{24}H_{30}O_2Br_2$. Calculated %: Br 31.35. 0.2041 g substance: 20.20 g C_6H_6: Δt 0.10°. Found: M 515.30. $C_{24}H_{30}O_2Br_2$. Calculated: M 509.83.

The obtained bromide is a fairly viscous, yellow liquid, with good solubility in acetone and chloroform, poor in alcohol. It does not decolorize bromine water and potassium permanganate solution. It gives a reaction for alkoxy groups (Zeisel), but on quantitative analysis the results are 3-5% less than the theoretical amount.

The analytical data for the prepared bromide of the butyl ether of diphenylbutynediol point to the formation of the dibromide of the olefinic series.

Bromination of the full isoamyl ether of diphenylbutynediol was carried out in a manner similar to that for the butyl ether, but using carbon tetrachloride instead of chloroform. The same results were obtained.

We had previously obtained similar results on bromination of the methyl, ethyl, propyl and isopropyl ethers of diphenylbutynediol.

III. Synthesis of Full Butyl and Isoamyl Ethers of Diphenylbutenediol (IIa and b) and Diphenylbutanediol (IIIb).

The esters of diphenylbutenediol were prepared by addition of 2 atoms of hydrogen to a molecule of the acetylenic ether (Ia and Ib) in presence of colloidal palladium; the esters of the saturated series were prepared by addition of 4 atoms of hydrogen in presence of platinum black.

Hydrogenation and isolation of the reaction products were performed by our previously described method [1]. The obtained ethers of the butenediol and the butanediol are light-yellow liquids, readily soluble in organic solvents.

Hydrolysis in an acid medium and the behavior toward bromine and potassium permanganate confirmed the structure of the full ethers of diphenylbutenediol and diphenylbutanediol. The properties of the synthesized ethers are set forth in Table 2.

SUMMARY

1. The following compounds were synthesized and characterized: The full butyl ether of diphenylbutynediol, the full butyl ether of diphenylbutenediol, the full isoamyl ether of diphenylbutynediol, the full isoamyl ether of diphenylbutenediol and the full isoamyl ether of diphenylbutanediol.

2. The action of bromine on the full butyl and isoamyl ethers of diphenylbutynediol was studied. It was shown that bromine adds on at the triple bond in the proportion of 2 atoms per molecule of acetylenic ether to form a bromoether of the olefinic series.

3. It was established that on hydrogenation of the full butyl and isoamyl ethers of diphenylbutynediol with colloidal palladium, the above-mentioned ethers of diphenylbutenediol can be isolated, while on hydrogenation with platinum black the ethers of diphenylbutanediol can be obtained.

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* See Consultants Bureau English Translation, p. 1873.

TERTIARY TRIHYDRIC ALCOHOLS OF THE ACETYLENIC SERIES AND THEIR TRANSFORMATIONS

II. SYNTHESIS OF 3,4,7-TRIMETHYL-5-OCTYNE-3,4,7-TRIOL, 2,5-DIMETHYL-5-(1-HYDROXYCYCLOHEXYL)-3-PENTYNE-2,5-DIOL, AND 2,4-DI-(1-HYDROXYCYCLOHEXYL)-3-BUTYNE-2-OL

V. I. Nikitin and S. D. Savranskaya

In an earlier paper [1] one of us described the synthesis of 2,3,6-trimethyl-4-heptyne-2,3,6-triol, the first simplest representative of a class of tertiary trihydric alcohols of the acetylene series.

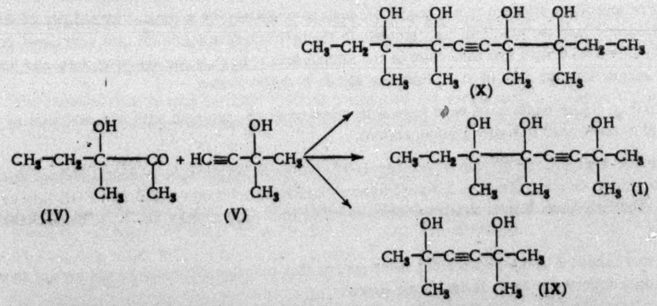
Monohydric alcohols of this series, as well as glycols, have been known for a long time, and many of them have found application not only in the laboratory but also in industrial organic synthesis. A. E. Favorsky and A. S. Onishchenko prepared and described a series of tertiary tetrahydric acetylenic alcohols – erythritols [2, 3]. Of the trihydric alcohols of the acetylenic series, only two primary-secondary alcohols are known:

$HC{\equiv}C{-}CHOH{-}CHOH{-}CH_2OH$ and $CH_2OH{-}C{\equiv}C{-}CHOH{-}CH_2OH$,

prepared by Lespieau via the organomagnesium synthesis [4, 5]. Respecting tertiary trihydric alcohols of the acetylenic series, these were completely unknown in the literature prior to the above-mentioned synthesis of trimethylheptynetriol.

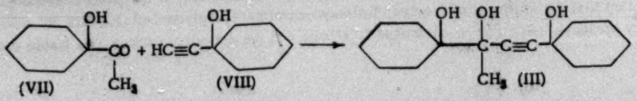
In the present paper we describe the synthesis of three more trihydric tertiary alcohols of the acetylenic series, starting from acetylenic alcohols and the corresponding hydroxy ketones.

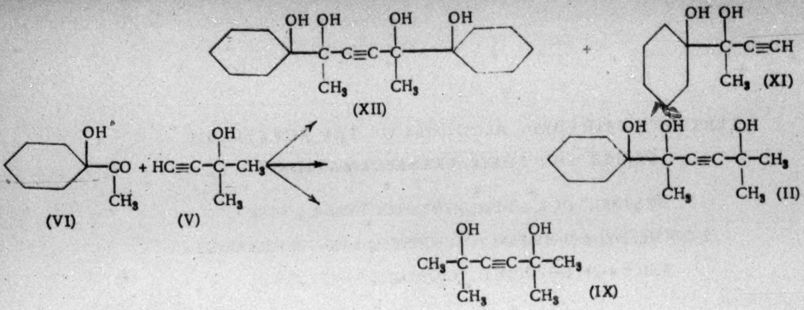
3,4,7-Trimethyl-5-octyne-3,4,7-triol (I) was prepared by condensation of methylethylacetylcarbinol (IV) with dimethylethinylcarbinol (V) according to the scheme:



2,5-Dimethyl-5-(1-hydroxycyclohexyl)-3-pentyne-2,5-diol (II) was prepared from acetylcyclohexanol (VI) and dimethylethinylcarbinol (V): (see next page)

2,4-Di-(1-hydroxycyclohexyl)-3-butyne-2-ol (III) was prepared by condensation of acetylcyclohexanol with ethinylcyclohexan-1-ol (VIII):





A close study of the preparation of these triols revealed the formation of a series of side products as indicated in the above reaction schemes; the detection of these products gives a clearer insight into the mechanism of the reaction.

In the first case, for example, products isolated, apart from 3,4,7-trimethyl-5-octyne-3,4,7-triol (I), were tetramethylbutynediol (IX) and the acetylenic erythritol, 3,4,7,8-tetramethyl-3,4,7,8-tetrahydroxy-5-decyne (X), previously described by A. S. Onishchenko. This author isolated two isomers of this compound with m.p. 111-112° and 155-156°. One of these is a racemate, the other a meso form. We only isolated one isomer with m.p. 155-156°.

In the second case, in addition to the tetrahydric alcohol, 2,5-dimethyl-5-(1-hydroxycyclohexyl)-3-pentyne-2,5-diol, the following were isolated: tetramethylbutynediol (IX), an α-glycol, 2-(1-hydroxycyclohexyl)-3-butyne-2-ol (XI), and a bicyclic erythritol, 2,5-di-(1-hydroxycyclohexyl)-3-hexyne-2,5-diol (XII), the latter not previously described in the literature. The erythritol contains two asymmetric atoms of carbon; we isolated two isomers with m.p. 161-162° and 147-149° (meso form and racemate).

In the third case no side products of reaction could be isolated.

A. I. Zakharova [6] synthesized nonsymmetrical acetylenic γ-glycols by the action of ketones on acetylenic carbinols in the conditions of the Favorsky reaction and obtained – apart from the expected glycol – two more symmetrically constructed acetylenic γ-glycols. These glycols, as Zakharova showed, are formed from the acetylene and the ketone – products of breakdown of the acetylenic alconols.

Formation of secondary products in our conditions may be explained by a similar breakdown of the acetylenic alcohol introduced into the reaction, i.e., breakdown of dimethylethinylcarbinol into acetylene and acetone. The free acetylene then reacts with two molecules of the ketoalcohol present in the reaction mass and forms an erythritol, in full accord with the data of A. E. Favorsky and A. S. Onishchenko.

Tetramethylbutynediol could have been formed by interaction of acetylene with two molcules of acetone, or by interaction of acetone with dimethylethinylcarbinol.

Concerning the α-glycol, 2-(1-hydroxycyclohexyl)-3-butyne-2-ol (XI), this is evidently formed during distillation in vacuum due to decomposition of 2,5-di-(1-hydroxycyclohexyl)-3-hexyne-2,5-diol (XII) into ketoalcohol and α-glycol. This decomposition is similar to that described by A. E. Favorsky and A. S. Onishchenko for other erythritols.

A. I. Zakharova showed in the above-cited investigation that acetylenic glycols do not appear to undergo decomposition, or only decompose to an insignificant extent.

Trihydric alcohols behave like glycols. We confirmed this by a special experiment. All the acetylenic triols that we obtained were, after 6 hours' stirring with KOH in a medium of dry ether at a temperature of −2 to −3° followed by standing for 12 hours at room temperature, almost completely recovered without any change whatever. In the same conditions monohydric alcohols are partly broken down to ketone and acetylene, from which are immediately formed the corresponding γ-glycols. The stability of the triols is demonstrated indirectly by the fact that the synthesis of 2,4-di-(1-hydroxycyclohexyl)-3-butyne-2-ol (III) was not accompanied by any secondary products; (III), like all monohydric alcohols of the acetylenic series, is a stable compound; the speed of its formation from acetylcyclohexanol and 1-ethinylcyclohexanol is so high that the acetylene and the cyclohexanol are able to react completely before any side reactions occur, thus giving the trihydric alcohol in high yield. Trihydric alcohols of the acetylenic series are only susceptible to breakdown under the action of alkaline reagents.

The structure of the so-obtained glycerols (I), (II), and (III), which are the main products of reaction, and the structure of the secondary products – the erythritols (X) and (XII) and the glycol (XI) – were verified by heating in presence of potassium carbonate when all the substances in question exhibited the characteristic property of tertiary acetylenic alcohols of breaking down into their original components. In all cases the corresponding hydroxyketones and acetylene were obtained.

EXPERIMENTAL

I. Synthesis of 3,4,7-Trimethyl-5-octyne-3,4,7-triol (I)

Starting materials: dimethylethinylcarbinol and methylethylacetylcarbinol were prepared by the usual methods.

The first was prepared by Favorsky's method: action of acetylene on acetone in presence of KOH in a medium of dry ether.

B.p. 99-101° at 695 mm; d_4^{20} 0.8614; n_D^{20} 1.4204. Found MR_D 24.70; $C_5H_8O|\equiv$. Calculated: MR_D 24.81.

The second was prepared by hydration of methylethylethinylcarbinol (Kucherov's method).

B.p. 148-149°; d_4^{20} 0.9402; n_D^{20} 1.4220. Found: MR_D 31.36. Calculated: MR_D 31.45.

A mixture of 23 g dimethylethinylcarbinol and 29 g methylethylacetylcarbinol in 75 ml absolute ether was run dropwise over a period of 3 hours into a flask fitted with a mechanical stirrer and containing 60 g chemically pure powdered KOH and 300 ml absolute ether. The flask was immersed in an ice bath at a temperature of −2 to −3°, which was maintained throughout the whole reaction period. With progressive addition of the mixture to the reaction flask, its contents thickened and became light-yellow. After the reaction mixture had been added, stirring was continued for a short period, after which the mass was left overnight. In the morning the formed complex had settled out as a light-yellow gelatinous mass which was decomposed with 30 ml water while stirring. The ethereal layer was then separated from the aqueous-alkaline layer; the latter was extracted several times with ether and the extracts combined into a single ethereal solution. This ether extract was saturated with carbon dioxide for 4 hours. After drying with sodium sulfate, the ethereal layer was filtered off and the ether distilled off. Weight of crude product 50 g. Fractionation of the latter in vacuum at 3 mm gave the following fractions: 1) 80-128°, 4.25 g, which crystallized; 2) 128-132°, 37.2 g, a viscous liquid; 3) 132-140°, 3.2 g crystals.

The first fraction with b.p. 80-128° at 3 mm consisted almost entirely of tetramethylbutynediol. After recrystallization from benzene it melted at 95-96°. The melting point was not depressed in admixture with an authentic specimen of tetramethylbutynediol.

The second fraction with b.p. 128-132° at 3 mm distilled over almost completely at 118-119° at 2 mm and proved to be 3,4,7-trimethyl-5-octyne-3,4,7-triol, the yield being 71.5 % based on the ketoalcohol taken in the reaction.

d_4^{20} 1.0239; n_D^{20} 1.4796. Found: MR_D 55.45. $C_{11}H_{20}O_3|\equiv$. Calculated MR_D 55.57.

3.260 mg substance: 7.849 mg CO_2; 3.002 mg H_2O. 8.334 mg substance: 20.096 mg CO_2; 7.720 mg H_2O. Found %: C 65.70, 65.80; H 10.37, 10.36. $C_{11}H_{20}O_3$. Calculated %: C 66; H 10. 0.0967 g substance: 37.8 ml CH_4 (19°, 692.1 mm). 0.0911 g substance: 36.2 ml CH_4 (20°, 692.1 mm). Found %: OH 25.30, 25.64. $C_{11}H_{20}O_3$. Calculated %: OH 25.51.

Cleavage of the triol (I) with potassium carbonate. 5.5 g substance was heated in a Wurtz flask in presence of 0.3 g potassium carbonate. Evolution of gas was observed and the gas was led through a side tube into ammoniacal silver oxide solution. When the gas was passed through an ammoniacal solution of cuprous chloride, the characteristic red color of copper acetylide was formed. The precipitate of silver acetylide was filtered off, dried and detonated by a blow. Three fractions were distilled: 1) 80-110°, 0.6 g; 2) 110-145°, 3.0 g; 3) 145-148°, 1.6 g.

In the first fraction were identified acetone (formation of a 2,4-dinitrophenyl-hydrazone with m.p. 124-125° which did not depress the m.p. of an authentic specimen of acetone phenylhydrazone) and dimethylethinylcarbinol (identified by the Kucherov hydration reaction which proceeded characteristically with intermediate formation of a white, curd-like precipitate which later went into solution with separation of metallic mercury).

In regard to the second and third fractions of decomposition products, boiling at 110-145° and 145-148°, these consisted of methylethylacetylcarbinol; the first of these, however, was contaminated with dimethylethinylcarbinol. Both of these fractions readily formed a semicarbazone (m.p. 150-151°) with semicarbazide hydrochloride and amixed test with authentic methylethylacetylcarbinol semicarbazone did not give a depression of melting point With 2,4-dinitrophenylhydrazine both fractions gave fine, yellow crystals melting (from ethyl alcohol) at 107-108° and not showing a depression in admixture with authentic methylethylacetylcarbinol phenylhydrazone.

The third fraction with b.p. 132-140° was recrystallized from a mixture of equal parts of benzene and ethyl alcohol. The crystals melted at 155-156° and corresponded to the erythritol, 3,4,7,8-tetramethyl-3,4,7,8-tetrahydroxy-5-decyne (X), first described by A. S. Onishchenko.

5.055 mg substance: 11.974 mg CO_2; 4.536 mg H_2O. 5.190 mg substance: 12.274 mg CO_2; 4.688 mg H_2O. Found %: C 64.62, 64.53; H 10.04, 10.11. $C_{14}H_{26}O_4$. Calculated %: C 65.11; H 10.08.

The prepared erythritol did not give a melting point depression with the authentic erythritol synthesized by the method of A. E. Favorsky and A. S. Onishchenko [2, 3] from methylethylethinylcarbinol and acetylene.

Decomposition of the erythritol (X) with m.p. 155-156° by heating with potassium carbonate. 2 g substance and a little potassium carbonate were heated in a small Wurtz flask. At the start of boiling a gas came off which, with ammoniacal silver oxide, gave a white precipitate of silver acetylide. The precipitate was filtered, dried, and detonated by impact. Into the receiver distilled a fraction with b.p. 146-148° (1.2 g) which was identified as methylethylacetylcarbinol (n_D^{20} 1.4209); with semicarbazide hydrochloride it readily forms a semicarbazone with m.p. 150-151° (from methyl alcohol), not giving a depression in admixture with authentic methylethylacetylcarbinol semicarbazide.

II. Synthesis of 2,5-Dimethyl-5-(1-hydroxycyclohexyl)-3-pentyne-2,5-diol (II)

The dimethylethinylcarbinol required for the synthesis was prepared as in the first case and had the same constants. Acetylcyclohexan-1-ol was prepared by hydration of 1-ethinylcyclohexan-1-ol by Kucherov's method and had the following constants: B.p. 52-53° at 3 mm; d_4^{20} 1.0217; n_D^{20} 1.4700. Found: MR_D 38.78. $C_{10}H_{14}O_2$. Calculated MR_D 38.48.

A mixture of 55 g acetylcyclohexanol and 32.5 g dimethylethinylcarbinol in 120 ml dry ether was run dropwise over a period of 4 hours into a flask containing 110 g chemically pure, pulverized KOH in 600 ml dry ether. The reaction conditions were the same as in the preceding synthesis. The solidified mass of reaction products was decomposed with water, during which process a small proportion failed to dissolve. The insoluble residue was filtered off. The ether layer was separated from the aqueous-alkaline layer; the latter was extracted 2-3 times with ether and the ethereal extract was combined with the original ethereal solution.

The precipitate which had not gone into solution in the ether gave, after several recrystallizations from methyl alcohol, colorless crystals with m.p. 161-162° (14.7 g), identifiable as the erythritol, 2,5-di-(1-hydroxycyclohexyl)-3-hexyne-2,5-diol (XII).

0.1643 g substance: 0.4188 g CO_2; 0.1456 g H_2O. 0.1289 g substance: 0.3290 g CO_2; 0.1135 g H_2O. Found %: C 69.52, 69.60; H 9.92, 9.90. $C_{18}H_{30}O_4$. Calculated %: C 69.67; H 9.68.

The structure of the substance was verified by cleavage during distillation in vacuum and over potassium carbonate. Its synthesis was also accomplished.

a) Cleavage of substance with m.p. 161-162° by vacuum distillation. 3 g substance was distilled in vacuum at 21-22 mm. A 2.3 g fraction boiling at 96-100° was collected. A second distillation of this at 20 mm gave 1.4 g with b.p. 99° which was identified as acetylcyclohexanol (n_D^{20} 1.4688). It forms a semicarbazone in the form of white needles, m.p. (from methyl alcohol) 194-195°, and did not give a depression of melting point with the semicarbazone of authentic 1-acetylcyclohexan-1-ol.

b) Cleavage of substance with m.p. 161-162° by heating with potassium carbonate. 2 g of the crystals was heated in a Wurtz flask at normal pressure in presence of a small amount of potassium carbonate; acetylene was evolved and was converted into silver acetylide by passage into ammoniacal silver oxide. Into a receiver was distilled a liquid fraction with b.p. 196-206° (1.5 g), which was 1-acetylcyclohexan-1-ol. When vacuum-distilled at 7-8 mm, the fraction came over almost completely at 80-82°; (n_D^{20} 1,4683). Its semicarbazone melted at 194-195° and did not depress the melting point of authentic acetylcyclohexanol semicarbazone.

c) Preparation of the erythritol, 2,5-di-(1-hydroxycyclohexyl)-3-hexyne-2,5-diol (XII) by the method of A. E. Favorsky and A. S. Onishchenko. For final proof of the structure of our isolated erythritol as symmetrical dimethyl-di-(1-hydroxycyclohexyl)-butynediol (XII), we prepared it by condensation of acetylcyclohexanol with acetylene.

To 400 ml dry ether and 56 g powdered KOH, through which a stream of acetylene was continuously passed, was added dropwise 30 g acetylcyclohexanol in 200 ml ether. The bath temperature was −5 to −10°. At the conclusion of the reaction, the reaction mass was treated with 50 ml water. The insoluble portion was separated and after recrystallization from ethyl alcohol it consisted of 26.1 g with m.p. 161-162°. A mixed melting test with the crystals that we prepared when synthesizing 2,5-dimethyl-5-(1-hydroxycyclohexyl)-2-pentyne-2,5-diol (II) did not show a depression.

The ethereal solution of the products of synthesis of the erythritol (XII) by the method of Favorsky and Onishchenko was separated from the aqueous-alkaline layer and dried; the ether was distilled off and the products distilled at 3-4 mm. A 2.4 g fraction with b.p. 60-110° was obtained (the residue of 1.5 g in the flask was not examined.)

The fraction with b.p. 60-110° (3mm) crystallized. The crystals melted at 67-68° (from ligroin) and a mixed melting test with the α-glycol 2-(1-hydroxycyclohexyl)-3-butyne-2-ol (XI) isolated in the synthesis of 2,5-dimethyl-5-(1-hydroxycyclohexyl)-3-pentyne)2,5-diol (II) did not give a melting point depression.

From the ethereal solution obtained by extraction of the products of synthesis of 2,5-dimethyl-5-(1-hydroxycyclohexyl)-3-pentyne-2,5-diol (II) was isolated a liquid which after vacuum fractionation (3 mm) gave four fraction: 1) 80-110°, 7.1 g, crystallized; 2) 110-151°, 5.4 g, a liquid; 3) 151-155°, 36.3 g, a viscous liquid which solidified to a transparent vitreous mass; 4) 155-210°, 1.5 g , crystallized.

The first fraction with b.p. 80-110° (3 mm) melted at 95-96° after recrystallization from benzene and corresponded to the tetramethylbutynediol (IX). No depression was found in the melting point determination of the mixture with authentic tetramethylbutynediol.

The second fraction with b.p. 110-151° (3 mm) gave after several redistillations: acetylcyclohexanol (VI) with b.p. 74-78° (5 mm), n_D^{20} 1.4693; semicarbazone with m.p. 193-195° which did not show a depression in admixture with the semicarbazone of authentic acetylcyclohexanol; also 4 g α-glycol, 2-(1-hydroxycyclohexyl)-3-butyne-2-ol (XI) with m.p. 67-68°. With ammoniacal silver oxide it forms a characteristic white precipitate indicating the presence of free acetylenic hydrogen.

0.1135 g substance: 0.2980 g CO_2; 0.0981 g H_2O. 0.1359 g substance: 0.3566 g CO_2; 0.1169 g H_2O. Found %: C 71.60, 71.55; H 9.67, 9.63. $C_{10}H_{16}O_2$. Calculated %: C 71.43; H 9.53. 0.0912 g substance: 29.3 ml CH_4 (23°, 700.4 mm). 0.0974 g substance: 30.8 ml CH_4 (22.9°, 699.1 mm). Found %: OH 20.77, 20.42. $C_{10}H_{16}O_2$. Calculated %: OH 20.23.

In the determination of the hydroxyl groups, the first measurement of the gas volume was taken because the gas volume progressively increased on standing, which indicates the presence of free acetylenic hydrogen.

The structure of the acetylenic α-glycol with m.p. 67-68° (XI) was confirmed by decomposition with potassium carbonate when acetylene was identified (precipitate when passed through ammoniacal silver oxide), also 1-acetylcyclohexan-1-ol which was characterized through the semicarbazone with m.p. 193-194°.

The third fraction with b.p. 151-155° (3 mm) was a viscous liquid which solidified on standing till the following day to form a light-green, vitreous mass which was then recrystallized from benzene. White crystals were obtained with m.p. 87-88° which were found to correspond to 2,5-dimethyl-5-(1-hydroxycyclohexyl)-3-pentyne-2,5-diol (II).

4.195 mg substance: 10.633 mg CO_2;3.700 mg H_2O. 4.640 mg substance: 10.788 mg CO_2; 4.078 mg H_2O. Found %: C 69.17, 69.33; H 9.87, 9.83. $C_{13}H_{22}O_3$. Calculated %: C 69.02; H 9.73. 0.0766 g substance: 26.8 ml CH_4 19.7°, 686.6 mm). 0.0886 g substance: 31.0 ml CH_4 (22.4°, 692.2 mm). Found %: OH 22.43, 22.41. $C_{13}H_{22}O_3$. Calculated %: OH 22.57.

Behavior toward KOH solution on heating. 5 g substance was heated under a reflux condenser with a solution of 3.5 g KOH in 25 ml water for 4 hours (until gas ceased to come off). With ammoniacal silver oxide the evolved gas forms a white precipitate of silver acetylide, while with ammoniacal cuprous chloride it forms a characteristic red precipitate of copper acetylide. The silver acetylide was filtered off, dried and detonated by a blow. The upper oily layer was extracted with ether, the extract was dried over sodium sulfate, the ether was driven off, and the residual product was distilled in vacuum (3 mm).

The first fraction with b.p. 52-53° weighed 2.9 g; the second fraction with b.p. 53-120° comprised a few drops. The 52-53° fraction, n_D^{20} 1.4690, was acetylcyclohexanol; it readily forms a semicarbazone which melts at 194-195° (from methyl alcohol) and does not give a depression with the semicarbazone of authentic 1-acetylcyclohexan-1-ol.

Consequently the fraction boiling at 151-155° (3 mm), in accord with the data obtained during its investigation, is the trihydric acetylenic alcohol — 2,5-dimethyl-5-(1-hydroxycyclohexyl)-3-pentyne-2,5-diol (II). Its yield, calculated on the acetylcyclohexanol taken in the reaction, is about 43% of the theoretical.

The fourth fraction with b.p. 155-210° at 3 mm was accumulated from several experiments. Recrystallization from benzene enabled two substances to be isolated: one with m.p. 147-149°, the other with m.p. 177-179°. The latter was present in such insignificant amount that it was not amenable to investigation. The compound with m.p. 147-149° corresponded to one of the isomers of 2,5-di-(1-hydroxycyclohexyl)-3-hexyne-2,5-diol (XII).

11.33 mg substance: 29.12 mg CO_2; 10.02 mg H_2O. 12.14 mg substance: 31.30 mg CO_2; 10.73 mg H_2O. Found %: C 70.30, 70.36; H 9.86, 9.88. $C_{18}H_{30}O_4$. Calculated %: C 69.67; H 9.68. 0.0728 g substance: 23.8 ml CH_4 (19.5°, 695.6 mm). 0.0692 g substance: 22.7 ml CH_4 (20.5°, 695.6 mm). Found %: OH 21.19, 21.24. $C_{18}H_{30}O_4$. Calculated %: OH 21.93.

On distillation in vacuum (4-4.5 mm), the substance with m.p. 147-149° broke down into acetylcyclohexanol (semicarbazone with m.p. 194-195°) and 2-(1-hydroxycyclohexyl)-3-butyne-2-ol (XI) with m.p. 67-68°.

Distillation of compound with m.p. 147-149° over potassium carbonate. The gas evolved when 2.6 g of the compound was heated with potassium carbonate was passed through ammoniacal silver oxide and formed silver acetylide. 1.4 g distilled off at 200-206° and formed a semicarbazone with m.p. 194-195° (1-acetylcyclohexan-1-ol).

Consequently, its elementary composition, its products of distillation in vacuum and its behavior with potassium carbonate identify the substance with m.p. 147-149° as the erythritol, 2,5-di-(1-hydroxycyclohexyl)-3-hexyne-2,5-diol (XII), which is isomeric with the erythritol with m.p. 161-162°.

III. Synthesis of 2,4- Di-(1-hydroxycyclohexyl)-3-butyne-2-ol (III)

The starting 1-ethinylcyclohexan-1-ol was prepared by the method of A. E. Favorsky and had the following constants:

B.p. 171-172° at 694 mm; m.p. 32-33°; d_4^{25} 0.9734, n_D^{25} 1.4808. Found: MR_D 36.24. $C_8H_{12}O$ F. Calculated: MR_D 36.42.

Acetylcyclohexanol was prepared as in the preceding synthesis and had the same constants.

A mixture of 53.5 g acetylcyclohexanol and 50 g ethinylcyclohexanol in 150 ml dry ether was run dropwise over a period of 5 hours into a flask containing 110 g chemically pure pulverized KOH and 600 ml dry ether. The reaction conditions and the working-up procedure were similar to those in the preceding syntheses. From the ethereal solution, after driving off the greater part of the ether, white crystals were deposited (89.3 g) which after recrystallization from ligroin melted at 107-108°; yield 86.3% of theory. From the mother liquor after removal of the solvent was recovered 5.6 g ethinyl cyclohexanol with b.p. up to 179° and n_D^{20} 1.4796, and 5.3 g acetylcyclohexanol, n_D^{20} 1.4688 and b.p. 179-205°.

The crystals with m.p. 107-108° were identified as the trihydric alcohol, 2,4-di-(1-hydroxycyclohexyl)-3-butyne-2-ol (III).

0.1894 g substance: 0.5006 g CO_2; 0.1706 g H_2O. 0.2248 g substance: 0.5944 g CO_2; 0.2034 g H_2O. Found %: C 72.07, 72.13; H 10.07, 10.13. $C_{16}H_{26}O_3$. Calculated %: C 72.18; H 9.77. 0.0742 g substance: 22.8 ml CH_4 (22.5°, 694.1 mm). Found %: OH 19.72. $C_{16}H_{26}O_3$. Calculated %: OH 19.17.

Decomposition of compound with m.p. 107-108° by heating with potassium carbonate. 5 g substance and a little potassium carbonate were heated in a Wurtz flask (fitted with a sloping condenser); gas was evolved and formed a white precipitate of silver acetylide with ammoniacal silver oxide and the characteristic red precipitate of copper acetylide with ammoniacal cuprous chloride.

In the receiver was collected 3.9 g liquid products boiling at 170-206°, fractionation of which gave: 0.3 g cyclohexanone (b.p. 154-155°, semicarbazone m.p. 166-167°) and 1-acetylcyclohexan-1-ol (b.p. 90-96° at 6 mm, n^{20}_D 1.4678, semicarbazone with m.p. 194-195°).

Consequently the substance obtained by condensation of 1-ethinylcyclohexan-1-ol with 1-acetylcyclohexan-1-ol corresponds to the tertiary trihydric acetylenic alcohol, 2,4-di-(1-hydroxycyclohexyl)-3-butyne-2-ol (III).

No by-products of this synthesis were isolated.

IV. Behavior of Tertiary Acetylenic Triols in the Conditions of the A.E. Favorsky Reaction

With the aim of establishing the mechanism of formation of the by-products, a study was made of the behavior of the synthesized acetylenic triols in the reaction conditions of their formation.

1) 42 g 3,4,7-trimethyl-5-octyne-3,4,7-triol in 100 ml dry ether was introduced into a flask containing 400 ml dry ether and 60 g chemically pure KOH. The mixture was stirred at a temperature of −2 to −3° for 6 hours and left overnight; the next day it was treated with water. The ethereal layer was separated and the ether was dried and driven off. The residual product was distilled in vacuum (2.5-3 mm) and was identified as the original alcohol; a fraction with b.p. 126-128°, weight 39.2 g, was collected; n^{20}_D 1.4789. Residue in flask 1.9 g. Loss 0.9 g.

2) 19.5 g 2,5-dimethyl-5-(1-hydroxycyclohexyl)-3-pentyne-2,5-diol (II) in 350 ml dry ether and 28 g KOH. Same conditions. 18 g of the substance was recovered unchanged.

3) 5 g 2,4-di-(1-hydroxycyclohexyl)-3-butyne-2-ol (III) in 150 ml dry ether and 10 g KOH. The original alcohol was recovered unchanged (4 g).

We may therefore conclude that trihydric alcohols, like glycols, are stable in the conditions of their synthesis, and that the formation of secondary products must result entirely from partial decomposition of the monohydric acetylenic alcohols described by A. I. Zakharova.

SUMMARY

1. Condensation of tertiary acetylenic alcohols with tertiary acetylcarbinols is a general method for preparation of tertiary trihydric acetylenic alcohols.

2. In addition to trihydric acetylenic alcohols, the reaction yields secondary products in the shape of other tertiary acetylenic alcohols: substituted butynediols, erythritols and α-glycols, due to partial breakdown of the original acetylenic carbinol.

3. The following tertiary trihydric acetylenic alcohols, not previously described in the literature, were prepared: 3,4,7-trimethyl-5-octyne-3,4,7-triol; 2,5-dimethyl-5-(1-hydroxycyclohexyl)-3-pentyne-2,5-diol; and 2,4-di-(1-hydroxycyclohexyl)-3-butyne-2-ol; two isomers of the acetylenic erythritol, 2,5-di-(1-hydroxycyclohexyl)-3-hexyne-2,5-diol, and one new acetylenic α-glycol, 2-(1-hydroxycyclohexyl)-3-butyne-2-ol.

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SYNTHESIS AND TRANSFORMATIONS OF SUBSTITUTED VINYL ETHERS

I. SYNTHESIS OF α-SUBSTITUTED VINYL ETHERS

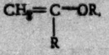
M. F. Shostakovsky and E. P. Gracheva

Among the unsaturated compounds susceptible to polymerization, special interest is attached to those containing diverse substituents. The effect of the latter is particularly conspicuous not only in respect of the character of the polymerization process but also in respect of the properties of the polymers. It is true that on the basis of our investigations [1] we established that a free-radical and ionic mechanism of polymerization, depending on the reaction conditions, may come into play for one and the same compound. Consequently one or the other form of polymerization is inherent in nearly all vinyl compounds, although observations show that one of them is more easily realized than the other. Ultimately, this depends not only on the structure of the vinyl compounds but also on the polymerization conditions.

Our present investigation is the first in a series devoted to the influence of substituents on the chemical properties and course of the polymerization reactions of substituted vinyl ethers.

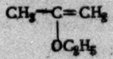
Previously we studied [2] the properties and transformations of vinyl ethers (I) which to a certain extent may be regarded as monosubstituted ethylenic derivatives, whereas α-substituted vinyl ethers are the corresponding disubstituted bodies (II)

(I) $CH_2=CH-OR$

(II)


$$CH_2=\underset{\displaystyle R}{\underset{|}{C}}-OR$$

An α-substituted vinyl ether was prepared for the first time by A. E. Favorsky in 1887 [3] during a study of the mechanism of isomerization of monosubstituted acetylenic hydrocarbons in presence of alcoholic KOH. On acting with alcoholic alkali on allylene, A. E. Favorsky obtained —in place of the anticipated propadiene — ethylisopropenyl ether (III):



$$CH_3-\underset{\displaystyle OC_2H_5}{\underset{|}{C}}=CH_2$$

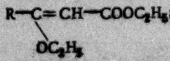
(III)

The same ether (III) was later prepared by Claisen [4] by another method, by heating ketals of acetone with phosphorus pentoxide and quinoline.

Moureau [5] considers that the action of alcohol on esters of fatty acids containing a triple bond in presence of the corresponding alcoholates is accompanied by addition of (IV), and that the alcohol (V) is split off on heating. On further heating of (V), these esters undergo hydrolysis with evolution of CO_2 and formation of α-substituted vinyl ethers (VI)

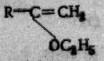
$R-C(OC_2H_5)_2CH_2COOC_2H_5$;

(IV)



$$R-\underset{\displaystyle \searrow OC_2H_5}{C}=CH-COOC_2H_5;$$

(V)



$$R-\underset{\displaystyle \searrow OC_2H_5}{C}=CH_2$$

(VI)

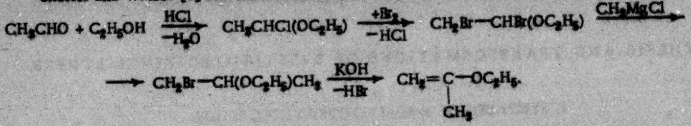
Heating of ethynylbenzene with alcohol in presence of concentrated solution of sodium alcoholate leads to formation of the α-substituted vinyl ether (VII), i.e., addition of alcohol takes place in the reverse order to that with compounds of the aliphatic series

$$C_6H_5CH=CH(OCH_3)$$

(VII)

We do not consider this observation to be adequately founded although we shall return to this question in our later communications.

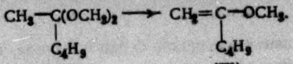
Sherril and Waller [6] obtained α-substituted vinyl ethers in accordance with the scheme:



$$CH_3CHO + C_2H_5OH \xrightarrow[-H_2O]{HCl} CH_3CHCl(OC_2H_5) \xrightarrow[-HCl]{+Br_2} CH_2Br-CHBr(OC_2H_5) \xrightarrow{CH_3MgCl}$$

$$\longrightarrow CH_2Br-CH(OC_2H_5)CH_3 \xrightarrow[-HBr]{KOH} CH_2=\underset{CH_3}{\underset{|}{C}}-OC_2H_5.$$

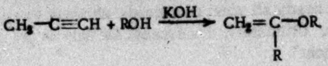
Hennion, Nieuwland and others [7] showed that on heating the ketal (VIII) with a small quantity of p-toluenesulfonic acid, it readily breaks down with loss of one molecule of alcohol to form the vinyl ether (IX)



$$\underset{(VIII)}{CH_3-\underset{C_4H_9}{\underset{|}{C}}(OCH_3)_2} \longrightarrow \underset{(IX)}{CH_2=\underset{C_4H_9}{\underset{|}{C}}-OCH_3.}$$

(VIII) (IX)

In this paper we present the synthesis of α-substituted vinyl ethers, starting from propyne and alcohols in presence of KOH. The synthesis was realized according to the scheme



$$CH_3-C{\equiv}CH + ROH \xrightarrow{KOH} CH_2=\underset{R}{\underset{|}{C}}-OR$$

TABLE 1

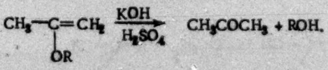
Structure and Constants of α-Substituted Vinyl Ethers

Prep. No.	α-Substituted vinyl ethers	B.p. (°C)	d_4^{20}	n_D^{20}	MR_D	
					Calc.	Found
1	$CH_3-\underset{OCH_3}{C}=CH_2$	28 (759 mm)	0.7372	1.3751	21.94	22.30
2	$CH_3-\underset{OC_2H_5}{\underset{|}{C}}=CH_2$	63-64 (749 mm)	0.7710	1.3913	26.65	26.92
3	$CH_3-\underset{OC_3H_7}{\underset{|}{C}}=CH_2$	78.5 (756 mm)	0.7861	1.3990	31.15	30.87

The reaction of propyne with alcohols proceeds in more drastic conditions than those established by A. E. Favorsky and M. F. Shostakovsky [8] for acetylene. Evidently the change from acetylene, containing two labile hydrogen atoms, to propyne is accompanied by a reduction in the ease of the addition reaction.

The general characteristics of the prepared α-substituted vinyl ethers are set forth in Table 1.

α-Substituted vinyl ethers constitute a class of compounds whose properties have not been closely studied. The conditions of hydrolysis of some members of the class have been studied. A. M. Butlerov [9], A. P. Eltekov [10] and A. E. Favorsky [11] have also studied the course of this reaction and have established the structure of the products of hydrolytic cleavage. The authors showed that hydrolysis of these compounds proceeds according to the scheme



$$CH_3-\underset{OR}{\underset{|}{C}}=CH_2 \xrightarrow[H_2SO_4]{KOH} CH_3COCH_3 + ROH.$$

We have utilized this reaction to verify the structure of the prepared α-substituted vinyl ethers.

EXPERIMENTAL

Starting Materials and Procedure for Synthesis

Starting materials were alcohols with the following constants:

1) Methyl alcohol: b.p. 63-64°; d_4^{20} 0.7941; n_D^{20} 1.3304.

2) Ethyl alcohol: b.p. 78.3°; d_4^{20} 0.7892; n_D^{20} 1.3623.

3) Propyl alcohol: b.p. 97.2°; d_4^{20} 0.8044; n_D^{20} 1.3854.

Propyne was selected as the monosubstituted acetylene. It was prepared by bromination of propylene followed by cleavage of two molecules of hydrogen bromide [12].

The so-prepared propyne was dried by passage through a column packed with calcium chloride, and was collected in a previously weighed receiver filled with carbon dioxide and placed in a Dewar flask.

The synthesis was effected in an autoclave. This was cooled to 0 to +2° (snow and salt), and the alcohols used were cooled to −10 to −15°. A definite quantity of propyne weighed into an ampoule was cooled with dry ice and was introduced in the ampoule into the autoclave containing the alcohol and the alkali.

1 Synthesis of α-Methylvinylmethyl ether: $CH_3C(OCH_3)=CH_2$

32 g (1 mole) methanol, 56 g (1.4 mole) propyne and 8.8 g 10% pulverized KOH were charged by the above procedure into a rotating autoclave of the Bergius type (capacity 1 liter), fitted with an electrical heater, a thermometer, and an acetylene gage. The autoclave was hermetically closed and heated for 18 hours at 220-225°. The dependence of the pressure on the temperature is shown in Table 2.

From the data of Table 2 we see that the pressure began to rise appreciably at 160-165°; at 225° it had reached 41 atm. This was followed by a marked fall in pressure in the autoclave. Prior to discharge, the autoclave was cooled (snow + salt). The propyne which had not reacted with the alcohol was collected in a trap placed in a Dewar flask containing carbon dioxide. 6.2 g propyne was collected. The remainder of the reaction mass was transferred from the autoclave to a small flask placed in a freezing mixture (snow + salt).

TABLE 2

Duration	Temp. in autoclave	Pressure in autoclave (in atm.)
0 hrs. 00 min.	20	6
0 hrs 40 min.	105	11.6
1 hr. 20 min.	135	14.6
2 hrs. 30 min.	165	24
3 hrs. 40 min.	200	38
	225	40.5
	225	41
6 hrs. 20 min.	225	39
	225	37.1

Fractionation of the reaction mass, which contained low-boiling products, was performed in a flask with a column on a water bath. The following fractions were collected: 1) b.p. 28° (759 mm), 31.2 g; 2) b.p. 63-64° (759 mm), 12.7 g; resinous residue, 5.7 g.

a) Examination of the fractions. The first fraction of 31.2 g was dried with calcined potassium carbonate and distilled in a column with an efficiency of 20 theoretical plates. A total of 30.2 g came over at 28° (759 mm), leaving traces of the original alcohol in the flask.

Constants of substance with b.p. 28°: n_D^{20} 1.3751; d_4^{20} 0.7372; found M 70.8 (cryoscopically in benzene). C_4H_8O. Calculated M: 72. Found MR_D 22.3. C_4H_8O. Calculated: MR_D 21.94.

Determination of the elementary composition by the combustion method is attended by serious difficulties which detract from the accuracy of the results. We prepared a polymer of the α-substituted vinyl ether and determined its elementary composition.

Found %: C 67.30; H 10.96. C_4H_8O. Calculated %: C 66.90; H 11.00.

The second fraction with b.p. 63-64° is unreacted methyl alcohol with n_D^{20} 1.3302; d_4^{20} 0.7990.

b) Hydrolysis of α-methylvinylmethyl ether. Into a conical flask with a ground glass stopper were introduced 15 g substance and 30 ml 1% H_2SO_4 solution. The reaction mixture was shaken for an hour at room temperature, after which the acid was neutralized with calcined potassium carbonate and the products of hydrolysis were fractionated in a plate column on a water bath. A 56-70° fraction was obtained, comprising a mixture of acetone and methyl alcohol.

Treatment of the mixture with 2,4-dinitrophenylhydrazine gave a precipitate of yellowish-orange crystals which after 2-3 recrystallizations from alcohol had m.p. 127.7°, the same as that of acetone 2,4-dinitrophenylhydrazone. No depression in mixed melting point test (the literature [13] gives m.p. 128°).

The characteristics of the 28° (759 mm) fraction show that reaction of propyne with methyl alcohol in presence of KOH gives α-methylvinylmethyl ether in a yield of about 30% of the theoretical.

2. Synthesis of α-Methylvinylethyl Ether: $CH_3C(OC_2H_5)=CH_2$

The preparation follows the procedure of the previous one.

Into a 1-liter rotating autoclave were charged 56 g (1.4 mole) propyne, 46 g (1 mole) ethyl alcohol, and 10 g KOH. The autoclave was heated for 18 hours at 210-220°. Appreciable rise of pressure set in at 160-170° and reached 37 atm, after which the pressure dropped. The unreacted propyne was collected in a trap (placed in a Dewar flask) after the autoclave had been cooled to room temperature. The Dewar flask was previously filled with carbon dioxide. 19.3 g propyne was collected. The remaining reaction mass was transferred to a small flask cooled with snow.

Fractionation of the reaction mass, which contained low-boiling products, was performed in a flask with a plate column on a water bath. The following fractions were collected: 1) b.p. 63-64° (749 mm), 46.2 g; 2) b.p. 77-78° (749 mm), 18.6 g; resinous residue, 11.7 g.

a). Examination of the fractions. The first fraction (63-64°) was dried with calcined potassium carbonate and distilled in a column with an efficiency of 20 theoretical plates. A total of 45.5 g came over at 64.1° (751 mm). The compound with b.p. 64.1° had the following constants:

n_D^{20} 1.3913; d_4^{20} 0.7710. Found: M (cryoscopically in benzene) 84.1. MR_D 26.92; Found %: C 69.48; H 11.33. $C_5H_{10}O$. Calculated: M 86; MR_D 26.65; Calculated %: C 69.76; H 11.63.

Literature data [6]: n_D^{20} 1.3913; d_4^{20} 0.7713.

The second fraction with b.p. 77-78° (749 mm) is unreacted ethyl alcohol with n_D^{20} 1.3621; d_4^{20} 0.7890.

b) Hydrolysis of α-methylvinylethyl ether. Hydrolysis was carried out in the above-described conditions. The obtained 2,4-dinitrophenylhydrazone had m.p. 127.4°, the same as that of acetone 2,4-dinitrophenylhydrazone. No depression in mixed test.

The examination of the 64.1° fraction shows that interaction of propyne with ethyl alcohol in presence of KOH leads to α-methylvinylethyl ether in a yield of 30.2% of the theoretical.

3. Synthesis of α-Methylvinylpropyl Ether: $CH_3C(OC_3H_7)=CH_2$.

Into the autoclave were charged 56 g (1.4 mole) propyne, 60 g (1 mole) propyl alcohol, and 10 g KOH. The autoclave was heated for 20 hours at 210-220°. After cooling to room temperature, 13.2 g unreacted propyne was discharged from the autoclave into a trap which was placed in a Dewar flask with carbon dioxide. The remaining reaction mass was transferred to a small flask cooled with snow.

The reaction mass was fractionated in a flask with a plate column (on a bath of Wood's alloy). The following fractions were collected: 1) b.p. 78° (756 mm), 54.2 g; 2) b.p. 97-99° (756 mm), 30.7 g.

a) Examination of the fractions. The 78° fraction was dried with calcined potassium carbonate and fractionated in a column with an efficiency of 20 theoretical plates. The whole of the fraction distilled at 78.5° (756 mm) and had n_D^{20} 1.3990, d_4^{20} 0.7861.

Found: M 102 (cryoscopically in benzene). MR_D 30.77. Found %: C 72.02; H 12.09. $C_6H_{12}O$. Calculated: M 100. MR_D 31.15. Calculated %: C 72.00; H 12.00.

The 97-99° fraction was unreacted propyl alcohol with n_D^{20} 1.3852; d_4^{20} 0.8041.

b) Hydrolysis of α-methylvinylpropyl ether. The 78.5° (756 mm) fraction was hydrolyzed under the conditions described above. Acetone 2,4-dinitrophenylhydrazone with m.p. 127.0° was obtained. Examination of the 78.5° fraction shows that the reaction of propyne with propyl alcohol in presence of KOH leads to α-methylvinylpropyl ether in a yield of 54% of the theoretical.

SUMMARY

1. The reaction of propyne with methyl, ethyl, and propyl alcohols in presence of pulverized potassium hydroxide leads to formation of α-substituted vinyl ethers: methylvinylmethyl, methylvinylethyl, and methylvinylpropyl ethers.

2. The structure of the α-substituted vinyl ethers was confirmed by their hydrolysis with 1% H_2SO_4 solution. The products of hydrolysis were isolated and characterized.

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FULL AND PARTIAL ESTERS OF β-FURYLACRYLIC ACID AND ETHYLENE GLYCOL

M. E. Egorova and M. A. Abramova

Intensive studies are now in progress in the field of synthesis of esters of acids of the acrylic series with aliphatic alcohols (mono- and polyhydric) as well as with cyclic alcohols.

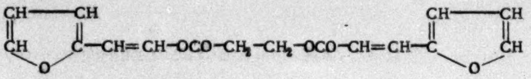
We set ourselves the task of establishing whether esters could be formed from polyhydric alcohols and β-substituted acids of the acrylic series. Esters of β-phenylacrylic acid with ethylene glycol have been prepared and described by us [1].

In the present investigation we established the possibility of formation of esters of ethylene glycol with β-furylacrylic acid. Esters of β-furylacrylic acid with polyhydric alcohols have not been described in the literature, although there are indications [2], that the presence of β-furylacrylic acid in a glycerol ester accelerates the drying of an oil and enhances the quality of the film.

We prepared esters of ethylene glycol with β-furylacrylic acid by the method of direct esterification at the ordinary pressure and a temperature of 150-200°, using an excess of one of the components.

EXPERIMENTAL

I. Preparation of Full Ester of β-Furylacrylic Acid and Ethylene Glycol



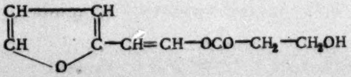
Into a flask, fitted with a gas discharge tube, were introduced ethylene glycol and β-furylacrylic acid (the latter prepared by oxidation of furfurylideneacetone with bleaching powder [3]) in the molar ratio of 1:3 and heated in an oil bath at a temperature of 180-200° for 3 hours. After neutralization with sodium carbonate solution, the residual crystalline product (dirty-yellow color) was separated and washed several times with water (the crystals became lighter in color). After two recrystallizations from alcohol (once in presence of animal charcoal), the product melted at 93-95°.

Found: M 299.1; %: C 63.45, H 4.69 saponification number 365.7. $C_{18}H_{14}O_6$. Calculated: M 302; %: C 63.57; H 4.63; saponification number 370.8.

The analytical data indicate that the crystalline product of reaction of ethylene glycol with β-furylacrylic acid is the full ester.

The product forms light-yellow crystals, readily soluble in acetone, benzene, ether and alcohol (on heating). Yield 48.9% of the theoretical.

II. Preparation of Partial Ester of β-Furylacrylic Acid and Ethylene Glycol



The appropriate amounts of acid and glycol (1:2 molar ratio) were placed in a flask fitted with a gas discharge tube and heated on an oil bath at 160-170° for 4 hours. The reaction product (dark-brown oil) was treated with benzene. The benzene extract was washed with sodium bicarbonate solution and water until neutral and then dried with calcined sodium sulfate. The benzene was distilled off and the residual mass distilled at 28-30 mm. The fraction coming over at 182-184° was analyzed.

Found: M 176.4; n_D^{25} 1.5678; saponification number 304.9; %: C 59.62; H 5.41. $C_9H_{10}O_4$. Calculated: M 182; saponification number 307.6; %: C 59.34; H 5.49.

The yield of purified product is 30-32% of the theoretical. The partial ester is a difficultly mobile, heavy (sp.gr. about 1.3) oil without odor and light-yellow in color; it has good solubility in benzene, alcohol, ether and acetone. In the air the oil quickly turns reddish-brown. When applied to glass in a thin layer, it forms a film (more quickly in the light) which is not lifted by benzene, alcohol or ether.

SUMMARY

The preparation of the full and partial esters of β-furylacrylic acid with ethylene glycol is described.

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INTERACTION OF TETRAPHENYLLEAD AND TETRAPHENYLTIN WITH CARBON TETRACHLORIDE IN PRESENCE OF BENZOYL PEROXIDE

Yu. A. Oldekop and R. F. Sokolova

G. A. Razuvaev [1], and later A. E. Borisov [2] showed that in presence of a small quantity of benzoyl peroxide or acetyl peroxide a reaction takes place between carbon tetrachloride and diphenylmercury. The reaction in Borisov's conditions is evidently of the homolytic, radical chain type since it is initiated by stoichiometrically small amounts of peroxides.

We thought it would be interesting to investigate this reaction more closely, and in this paper we have attempted to establish whether the reaction takes place between carbon tetrachloride and phenyl derivatives of other metals. For this purpose we selected tetraphenyllead and tetraphenyltin. These compounds are known to react with carbon tetrachloride under the influence of ultraviolet light [3].

No reactions were observed on prolonged boiling of solutions of tetraphenyllead or tetraphenyltin in carbon tetrachloride in presence of small amounts of a peroxide. Obviously no chain reaction took place. We therefore considerably increased the amount of peroxide; reaction then took place. In these conditions the main reaction product with tetraphenyllead (in presence of benzoyl peroxide) is diphenyllead dichloride; a small amount of diphenyllead dibenzoate is also formed.

Hence the process of dearylation in the case of tetraphenyllead stops at compounds of the type of Ar_2PbX_2.

Other reaction products were chlorobenzene (identified by conversion to 2,4-dinitrochlorobenzene), hexachloroethane, and benzoic and phthalic acids.

On the basis of the above data, we may represent the reaction course by the following scheme:

$$(C_6H_5CO_2)_2 \longrightarrow C_6H_5\cdot + CO_2 + C_6H_5COO\cdot$$

$$CCl_4 + C_6H_5\cdot \longrightarrow C_6H_5Cl + CCl_3\cdot$$

$$(C_6H_5)_4Pb + CCl_3\cdot \longrightarrow (C_6H_5)_3Pb\cdot + C_6H_5CCl_3$$

$$(C_6H_5)_3Pb\cdot + CCl_4 \longrightarrow (C_6H_5)_3PbCl + CCl_3\cdot$$

$$(C_6H_5)_3PbCl + CCl_3\cdot \longrightarrow (C_6H_5)_2PbCl\cdot + C_6H_5CCl_3$$

$$(C_6H_5)_2PbCl\cdot + CCl_4 \longrightarrow (C_6H_5)_2PbCl_2 + CCl_3\cdot$$

$$2CCl_3\cdot \longrightarrow Cl_3C{-}CCl_3.$$

Benzoic acid may originate from saponfication of $C_6H_5CCl_3$.

The presence of diphenyllead dibenzoate among the reaction products may be explained by the following scheme:

$$(C_6H_5)_3Pb\cdot + C_6H_5COO\cdot \longrightarrow (C_6H_5)_3PbOCOC_6H_5$$

$$(C_6H_5)_3PbOCOC_6H_5 + CCl_3\cdot \longrightarrow C_6H_5CCl_3 + (C_6H_5)_2\dot{P}bOCOC_6H_5$$

$$(C_6H_5)_2PbOCOC_6H_5 + C_6H_5COO\cdot \longrightarrow (C_6H_5)_2Pb(OCOC_6H_5)_2.$$

The reaction between tetraphenyltin and carbon tetrachloride was performed in similar conditions in presence of benzoyl peroxide.

Since the disubstituted tin derivatives of the type of Ar_2SnX_2 are very highly soluble, in this case we get complete dearylation of tetraphenyltin with formation of tin tetrachloride.

Other products of the reaction were chlorobenzene (identified by the usual method), hexachloroethane, and benzoic and phthalic acids. A reaction scheme similar to that proposed above for tetraethyllead could be proposed for the tin compound, except that here the process of dearylation proceeds to completion, to $SnCl_4$.

The only point that still remains obscure is the mechanism of formation of benzoic acid, which could proceed via the phenyl radical, the peroxide or the organometallic compound itself. This problem might be solved by carrying out these reactions in presence of acetyl peroxide.

EXPERIMENTAL

Reaction of Tetraphenyllead with Carbon Tetrachloride in Presence of Benzoyl Peroxide

Into a round-bottomed flask fitted with a condenser (ground-glass joint) was charged a solution of 5.0 g tetraphenyllead in 100 ml carbon tetrachloride. While the reaction mass was boiling, the benzoyl peroxide was introduced in small portions over a period of 8 hours (total amount of peroxide 20 g). After the whole of the peroxide had been added, the reaction mass was boiled for another 50 hours. At the conclusion of the reaction (test with KI for peroxide) the cooled solution was filtered from the precipitate which consisted of $(C_6H_5)_4Pb$ and $(C_6H_5)_2PbCl_2$.

The precipitate was washed with hot toluene which dissolved the tetraphenyllead; after recrystallization from the same solvent it melted at 225°. It did not depress the melting point of authentic tetraphenyllead. Weight 1.7 g, or 34% of the original amount. The toluene-insoluble portion of the precipitate was $(C_6H_5)_2PbCl_2$. Its weight was 2.55 g or 60.8% of the theoretical amount.

Found %: Pb 48.23, 48.12, 48.48. $C_{12}H_{10}PbCl_2$. Calculated %: Pb 47.85.

The filtrate was made alkaline with KOH and distilled with steam. At the termination of the distillation, crystals of hexachloroethane with m.p. 186° (sealed capillary) were extracted from the condenser. There was no melting point depression in admixture with authentic hexachloroethane. Weight 2.43 g.

After removal of water, the distillate was nitrated. A nitro compound was isolated with m.p. 51-52° (from alcohol), weight 1.8 g. There was no melting point depression in a test of this substance with authentic 2,4-dinitrochlorobenzene.

The residue from the steam distillation was filtered and a further small quantity of tetraphenyllead was recovered from it. The main mass of this substance, after recrystallization from alcohol, had m.p. 228-229°. Weight 0.31 g of 5.2% of the theoretical amount. A mixed melting test with the substance prepared specially from tetraphenyllead and benzoic acid likewise gave m.p. 228-229°. This substance was therefore diphenyllead benzoate, as was confirmed by the lead determination.

Found %: Pb 34.34, 34.48. $C_{26}H_{20}O_4Pb$. Calculated %: Pb 34.35.

Addition of hydrochloric acid to the filtrate brought down a white precipitate weighing 2.42 g. This was filtered and dissolved in hot water. The main mass dissolved and had m.p. 120° (from alcohol). A mixture with authentic benzoic acid also had m.p. 120°.

The small quantity of water-insoluble acids contained phthalic acid, as shown by the characteristic fluorescence when fused with resorcinol.

Reaction of Tetraphenyltin with Carbon Tetrachloride in Presence of Benzoyl Peroxide

The reaction of tetraphenyltin with carbon tetrachloride in presence of benzoyl peroxide was effected in conditions substantially similar to those for tetraphenyllead. Reaction components were 5.0 g tetraphenyltin, 10.0 g benzoyl peroxide and 100 ml carbon tetrachloride. At the end of the reaction (50 hours) the precipitate was filtered off and identified as unreacted tetraphenyltin (m.p. 224-225°) which did not give a depression with authentic, pure tetraphenyltin. Weight 0.21 g or 4.2% of the original.

Solvent was removed from the filtrate by distillation on a water bath. The tin chloride formed during the reaction was determined in the form of tin disulfide by precipitation with hydrogen sulfide. The total yield of $SnCl_4$ was 84.1% of the theoretical.

A special experiment was run for the purpose of isolation of the remaining products of reaction (non-organometallic). In this case, alkali was added to the filtrate and steam was passed through. Hexachloroethane with m.p.

186° was isolated. It did not give a depression in a mixed test with authentic material. Weight 2.6 g. The distillate was nitrated and worked up in the usual manner to give a nitro compound with m.p. 51-52°. Weight 1.8 g. This substance did not give a depression of m.p. with pure 2,4-dinitrochlorobenzene. Benzoic acid (2.1 g) and phthalic acid were identified by the same tests as in the previous experiment.

SUMMARY

1. It was shown that interaction of tetraphenyllead with carbon tetrachloride in presence of benzoyl peroxide leads to partial dearylation of tetraphenyltin with formation of compounds of the type of $(C_6H_5)_2PbX_2$, sparingly soluble in organic solvents. Other identified reaction products were chlorobenzene, hexachloroethane and benzoic and phthalic acids.

2. The corresponding reaction of tetraphenyltin with carbon tetrachloride in presence of benzoyl peroxide results in complete dearylation of tetraphenyltin with formation of tin tetrachloride. Other reaction products were chlorobenzene, hexachloroethane, and benzoic and phthalic acids.

3. In conclusion we extend our deep gratitude to G. A. Razuvaev for his constant interest and valuable assistance in the investigation.

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THE SELECTIVE MALONIC SYNTHESIS

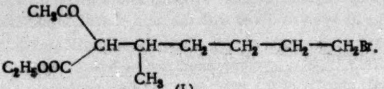
IV. THE ACTION OF SODIO-MALONIC ESTER ON 1,5-DIBROMOHEXANE

V. P. Golmov

In the previous papers [1,2,3,4,5] we reported the results of investigations of the interaction of sodio-malonic ester with dihalo derivatives of symmetrical structure (trimethylene bromide, tetra- and pentamethylene bromides, 2,5-dibromohexane, hexamethylene iodide, and a number of others).

A fairly large number of researches are known in which are described reactions between sodio-malonic (or sodio-acetoacetic) ester and dihalo derivatives of unsymmetrical structure (1,3-dibromobutane [6], 1,5-dibromohexane [7], etc.). The mechanism of these reactions has never been investigated, the literature therefore being lacking in any information on, for example, which of the two bromine atoms (attached to the primary or secondary carbon atom) is the first to enter into reaction with sodio-malonic ester.

Only isolated conjectures about the course have been suggested. Thus, for example, Perkin, Jr. [7], in acting with sodio-acetoacetic ester on 1,5-dibromohexane in equimolar ratios, assigned the structure of (I) to the product without giving any proof:

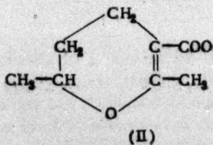


$$(CH_3CO)(C_2H_5OOC)CH-CH(CH_3)-CH_2-CH_2-CH_2-CH_2Br.$$

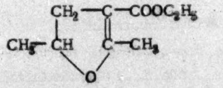
(I)

He assumed that the atom of bromine attached to the secondary carbon atom must be the first to enter into reaction.

In another research, however, the same author [8] reacted sodio-acetoacetic ester with 1,3-dibromobutane and obtained 2,6-dimethyl-5,6-dihydropropane-3-carboxylic ester (II). Lipp and Scheller [9] showed that in the action of sodio-acetoacetic ester on propylene bromide, 2-methyl-1-acetylcyclopropane-1-carboxylic ester and the ester of β-methyl-α,α'-diacetyladipic acid are formed, but also the ester of 2,5-dimethyl-4,5-dihydrofuran-3-carboxylic acid (III)

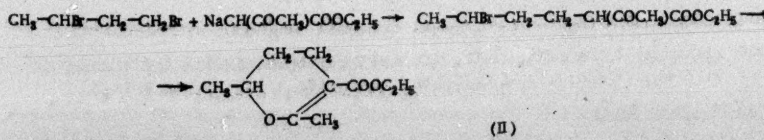


(II)



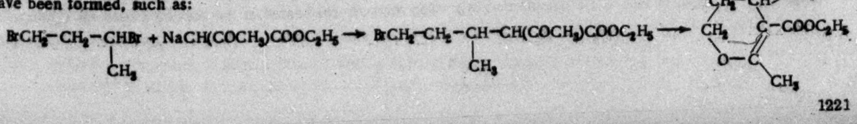
(III)

It is not difficult to see that the formation of these substances must be preceded by the formation of bromoalkylacetoacetic esters with the atom of bromine at the secondary carbon atom, for example



(II)

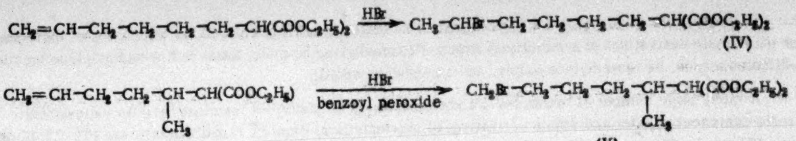
If the reaction should proceed differently in the first stage, then products with a different structure would have been formed, such as:



In this research we have investigated the action of sodio-malonic ester on 1,5-dibromohexane for the purpose of establishing which of the two atoms of bromine in the molecule of an unysmmetrical dihalo derivative is the first to react with sodio-malonic ester.

In this investigation an intermediate product was obtained in the shape of bromohexylmalonic ester which could be either ϵ-bromohexylmalonic ester (IV) or ϵ-bromo-*a*-methyl-amylmalonic ester (V).

In order to verify its structure, both the latter compounds were synthesized by another route, namely, by addition of HBr to ϵ-hexenylmalonic ester which was synthesized for this purpose by the action of sodio-malonic ester on 6-bromo-1-hexene (for compound IV), and by addition of HBr in presence of benzoyl peroxide to the previously [3] prepared *a*-methyl-δ-pentenylmalonic ester (for compound V):



$$CH_2{=}CH{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}CH(COOC_2H_5)_2 \xrightarrow{HBr} CH_3{-}CHBr{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}CH(COOC_2H_5)_2$$

(IV)

$$CH_2{=}CH{-}CH_2{-}CH_2{-}\underset{\displaystyle CH_3}{\underset{|}{CH}}{-}CH(COOC_2H_5)_2 \xrightarrow[\text{benzoyl peroxide}]{HBr} CH_2Br{-}CH_2{-}CH_2{-}CH_2{-}\underset{\displaystyle CH_3}{\underset{|}{CH}}{-}CH(COOC_2H_5)_2$$

(V)

The structure of both compounds was confirmed by the formation from them, by the action of sodium ethylate, of 1-methylcyclohexane-2,2-dicarboxylic acid ester.

The two prepared bromoesters differed fairly sharply in physical constants and behaved quite diversely under the action of sodium alcoholate.

Whereas ϵ-bromo-*a*-methyl-amylmalonic ester is converted into 1-methylcyclohexane-2,2-dicarboxylic ester in a yield of 70% of the theoretical when cyclized with the help of sodium alcoholate, ϵ-bromohexylmalonic ester in the same conditions is cyclized with a yield of only 5% of the theoretical. Only by working in very dilute solution was it possible to convert it into 1-methylcyclohexane-2,2-dicarboxylic ester in a yield of about 45% of the theoretical. In the latter case, a small amount of the ethyl ester of ϵ-ethoxyhexylmalonic acid is also formed.

The bromohexylmalonic ester prepared by the action of sodio-malonic ester on 1,5-dibromohexane is completely identical in its constants and behavior on cyclization with ϵ-bromohexylmalonic ester, and it is therefore extremely probable that it has the same structure.

EXPERIMENTAL

The 1,5-dibromohexane required for the research was prepared by the method of Perkin, Jr. [10]; action of HBr on 1,5-hexanediol. The prepared starting material had b.p. 93-96° at 5 mm [11].

Action of Sodio-malonic Ester on 1,5-Dibromohexane

To a solution of alcoholate, prepared from 5.7 g (0.24 g-atom) metallic sodium and 75 ml absolute alcohol, was added 115 g (0.72 mole or three times more than the theoretically calculated amount) malonic ester, and then 59 g (0.24 mole) 1,5-dibromohexane. The liquid was heated to boiling on a bath for 6 hours; it was then cooled and water was added; the resultant oil was extracted with ether and the ether extract was washed with water and dried with calcined calcium chloride; the ether was then driven off and the residue fractionated in vacuum. The excess of malonic ester came over first (80° (5 mm) fraction), followed by a fraction with b.p. 153-180° (3 mm) consisting of bromohexenylmalonic ester in the form of a colorless, oily liquid with the characteristic odor of a bromoalkyl malonic ester. A considerable residue remained in the flask. On redistillation this fraction boiled mainly at 160-161° (3 mm).

d_4^{20} 1.2073; n_D^{20} 1.4612; MR_D 73.45. $C_{13}H_{23}O_4Br$. Calculated: MR_D 73.31.

0.2360 g substance: 0.4192 g CO_2; 0.1472 g H_2O. 0.3472 g substance: 0.2003 g AgBr (Carius).
Found %: C 48.44; H 6.92; Br 24.54. $C_{13}H_{23}O_4Br$. Calculated %: C 48.30; H 7.12; Br 24.69.

ϵ-Hexenyl Malonic Ester

To a solution of alcoholate, prepared from 10.4 g (0.45 g-atom) metallic sodium and 120 ml absolute alcohol, was added first 144 g (0.9 mole) [12] malonic ester and second 73 g (0.45 mole) 6-bromo-1-hexene (prepared by addition of HBr to 1,5-hexadiene [13]). The mixture was heated at the boil on a bath for 6 hours; after cooling, it was then poured into water acidified with hydrochloric acid; the reaction products were extracted with ether and the ether extract was washed with water and dried with calcined calcium chloride; the ether was driven off and the residue subjected to fractional distillation in vacuum in a column. Malonic ester, b.p. 80° at 4 mm (74.5 g) first came over; the thermometer then rose rapidly and at 120-121° (4 mm) 30 g ε-hexenylmalonic ester came over (73.4% of the theoretical).

After a second distillation the product boiled at 114-115° (2 mm) and consisted of a colorless, almost odorless liquid.

d_4^{20} 0.9755; n_D^{20} 1.4390; MR_D 65.25. $C_{13}H_{22}O_4\vDash$. Calculated: MR_D 65.08.

0.2574 g substance: 0.6072 g CO_2; 0.2133 g H_2O. Found %: C 64.34; H 9.20. $C_{13}H_{22}O_4$.
Calculated %: C 64.46; H 9.09.

12 g of the substance was saponified with a solution of 10 g KOH in 50 ml 95% alcohol with heating for 1½ hours. The liquid was then diluted with water, the alcohol was completely distilled off on a water bath, and the residue (cooled) was acidified with dilute H_2SO_4 and extracted 5 times with ether. The ether extract was dried with ignited calcium chloride and the ether distilled off to leave 8.9 g (96.5% of the theoretical) of crystalline ε-hexenylmalonic acid. After two recrystallizations from benzene it melted at 79°.

0.2042 g substance: 0.4352 g CO_2; 0.1368 g H_2O. Found %: C 58.12; H 7.44. $C_9H_{14}O_4$.
Calculated %: C 58.06; H 7.53.

ε-Hexenylmalonamide was prepared by the action of aqueous ammonia (s.g. 0.88) on ε-hexenylmalonic ester at the ordinary pressure for several days, using the method of Demyanov and Telnov [14]. After recrystallization from water it melted at 195-196°.

0.1336 g substance: 14.4 ml 0.1 N H_2SO_4 (Kjeldahl). Found %: N 15.09. $C_9H_{16}O_2N_2$.
Calculated % N 15.21.

7.8 g ε-hexenylmalonic acid was heated under a reflux condenser on a bath of Wood's alloy at 180-200° until CO_2 ceased to come off. The 1-octene-8-carboxylic acid remaining after decarboxylation distilled at 234-236° (706 mm). The yield was 4.9 g or 83.1% of the theoretical.

d_4^{20} 0.9348; n_D^{20} 1.4430; MR_D 40.27. $C_8H_{14}O_2\vDash$. Calculated: MR_D 40.21.

0.2706 g substance: 0.6677 g CO_2; 0.2456 g H_2O. Found %: C 67.29; H 10.08. $C_8H_{14}O_2$.
Calculated %: C 67.60; H 9.86.

1-Octene-8-carboxylamide was prepared by the usual method via the acid chloride by acting on the latter in solution in dry ether with gaseous ammonia. After recrystallization from chloroform it melted at 75-76°.

0.1080 g substance: 7.64 ml 0.1 N H_2SO_4 (Kjeldahl). Found %: N 9.90. $C_8H_{15}ON$. Calculated %: N 9.92.

ε-Bromohexylmalonic Ester

Into 58 g (0.24 mole) ε-hexenylmalonic ester (cooled with snow and salt) was passed 22 g (0.27 mole) of moist [17] hydrogen bromide. The mixture was left at room temperature for 24 hours and then poured into water; the reaction product was separated, washed with water, dried with ignited calcium chloride, and distilled in vacuum, when the whole came over at 160-161° (3mm). Yield 72.5 g, or 92.1% of the theoretical.

d_4^{20} 1.2084; n_D^{20} 1.4619; MR_D 73.40. $C_{13}H_{23}O_4Br$. Calculated: MR_D 73.31.

0.3148 g substance: 0.5562 g CO_2; 0.2042 g H_2O. 0.3583 g substance: 0.2063 AgBr (Carius).
Found %: C 48.19; H 7.21; Br 24.49. $C_{13}H_{23}O_4Br$. Calculated %: C 48.30; H 7.12; Br 24.69.

The substance is a colorless, heavy liquid with the odor of a bromoalkylmalonic ester.

ε-Bromo-α-methylamylmalonic Ester

To 42.5 g (0.17 mole) of α-methyl-δ-pentenylmalonic ester [3] was added 0.2 g benzoyl peroxide and about 20.0 g of dry HBr was introduced while cooling with ice and salt. The mixture was left at room temperature for 24 hours, then poured on to water; the lower layer was separated, washed with water, dried with ignited calcium chloride, and distilled in vacuum. Nearly the whole came over at 156-157° (3 mm). Yield 46 g, or 83.8% of the theoretical.

d_4^{20} 1.2143; n_D^{20} 1.4630; MR_D 73.34. $C_{13}H_{23}O_4Br$. Calculated: MR_D 73.31.

0.2164 g substance: 0.3820 g CO_2; 0.1382 g H_2O. 0.3938 g substance: 0.2258 g AgBr (Carius).
Found %: C 48.15; H 7.10; Br 24.40. $C_{13}H_{23}O_4Br$. Calculated %: C 48.30; H 7.12; Br 24.69.

Cyclization of ε-Bromo-α-methylamylmalonic Ester

2.3 g (0.1 g-atom) metallic sodium was dissolved in 50 ml absolute alcohol and to the alcoholate solution was added (with cooling) 32.2 g ε-bromo-α-methylamyl-malonic ester. The initial concentration of the reacting substance was 1.3 molar. The mixture was heated on a bath at the boil for 4 hours and then cooled, poured into water; the reaction product was extracted several times with ether and the ether extract was washed with water, and dried with ignited calcium chloride; the ether was driven off and the residue was fractionated in vacuum to give 15.5 g with b.p. 116-117° (5 mm) and 5 g residue. The yield was 72.3% of the theoretical.

d_4^{20} 1.0312; n_D^{20} 1.4506; MR_D 63.14. $C_{13}H_{22}O_4$. Calculated: MR_D 63.34.

0.2728 g substance: 0.6435 g CO_2; 0.2244 g H_2O. Found %: C 64.36; H 9.13. $C_{13}H_{22}O_4$.
Calculated %: C 64.47; H 9.09.

The substance was saponified with 20% alcoholic KOH for 1½ hours, after which the liquid was diluted with water and the alcohol distilled off. The residue, after cooling, was acidified with dilute sulfuric acid and repeatedly extracted with ether. The ethereal extract was dried with ignited calcium chloride and the solvent was driven off, leaving the dicarboxylic acid in the form of a thick oil which partly crystallized after lengthy standing in a desiccator over sulfuric acid. The crystals were drained, pressed on a porous plate and twice recrystallized from a small quantity of formic acid. M.p. 154-155°. According to Perkin [15], 1-methylcyclohexane-2,2-dicarboxylic acid melts at 147°.

0.1084 g substance: 0.2303 g CO_2; 0.0746 g H_2O. Found %: C 57.94; H 7.65. $C_9H_{14}O_4$.
Calculated %: C 58.06; H 7.53.

The other portion of the 1-methylcyclohexane-2,2-dicarboxylic acid, immediately after isolation from the ethereal solution, was heated in Wood's alloy to 200° and transformed into cis-hexahydro-o-toluic acid, which, on distillation, boiled at 230-235° [16]. The latter was converted, via the acid chloride, into the amide which melted at 150-152° after two recrystallizations from dilute methyl alcohol [16].

Cyclization of ε-Bromohexylmalonic Ester

The experiments described below were performed both with ε-bromohexylmalonic ester prepared by addition of HBr to ε-hexenylmalonic ester and with the bromoester prepared by reaction of sodio-malonic ester with 1,5-dibromohexane. In both cases identical results were obtained.

First experiment. To a solution of alcoholate prepared from 1.6 g (0.07 g-atom) metallic sodium and 35 ml absolute alcohol was added 21.5 g (0.067 mole) ε-bromohexylmalonic ester. The initial concentration of the reacting substance was 1.26 molar. The mixture was heated at the boil on a bath for 5 hours, after which addition was made to it (with cooling) of water acidified with hydrochloric acid; the resultant oil was extracted with ether and the ethereal extract was washed with water and dried with ignited calcium chloride; the ether was distilled off. Vacuum distillation of the residue gave a total distillate of 0.8 g, boiling at 124-126° (6 mm). The residue in the flask was about 15 g viscous, dark oil which could not be distilled without decomposition. The 124-126° fraction was, as shown below, 1-methylcyclohexane-2,2-dicarboxylic ester. Yield 5% of the theoretical.

Second experiment. 16.2 g (0.05 mole) bromoester was added to a solution of alcoholate prepared from 1.15 g (0.05 g-atom) metallic sodium and 287 ml absolute alcohol. The initial concentration in this case was 0.17 molar. After heating at the boil on a bath for 5 hours, distillation of the greater part of the alcohol, and further working-up in the above-described manner, 3.8 g 1-methylcyclohexane-2,2-dicarboxylic ester with b.p. 125-131° (8 mm) was obtained (31.4% of the theoretical), as well as 2.2 g of a fraction coming over at 131-170° (8-9 mm). The residue in the flask was a fairly large amount of viscous, dark liquid.

Third experiment. In order not to excessively increase the volume of the reacting mixture, to the alcoholate solution prepared from 1.0 g (0.043 g-atom) metallic sodium and 250 ml absolute alcohol (heated to boiling) was added 14 g (0.043 mole) ε-bromohexylmalonic ester in 10 portions of 1.4 g each. After each addition the initial concentration of the reacting substance was 0.017 molar. After each addition the liquid was boiled on a bath for an hour. After working up as in the second experiment, vacuum fractionation gave 4.7 g (45.2 % of the theoretical) 1-methylcyclohexane-2,2-dicarboxylic ester with b.p. 124-131° (8 mm), also 1.5 g of a fraction with boiling range 131-170°. The 124-131° fractions from the three experiments were combined and after a fresh distillation in vacuum the liquid boiled (mainly) at 110-114° (3 mm).

d_4^{20} 1.0296; n_D^{20} 1.4490; MR_D 63.11. $C_{13}H_{22}O_4$. Calculated: MR_D 63.34.

0.2692 g substance: 0.6385 g CO_2; 0.2262 g H_2O. Found %: C 64.69; H 9.33. $C_{13}H_{22}O_4$. Calculated %: C 64.49; H 9.12.

The ester of 1-methylcyclohexane-2,2-dicarboxylic acid was saponified with alcoholic KOH and the resultant 1-methylcyclohexane-2,2-dicarboxylic acid (a thick oil) was decarboxylated to form cis-hexahydro-o-toluic acid with b.p. 230-236°. The amide was prepared as above and after two recrystallizations from dilute methyl alcohol it had m.p. 151-152° [16].

The 131-170° fraction obtained in the second and third experiments was redistilled in vacuum to give about 2 g substance with b.p. 148° (3 mm).

The physical constants and the elementary analysis of this substance indicate that it is probably the ethyl ester of ε-ethoxyhexylmalonic acid, formed as a by-product during the action of sodium alcoholate on ε-bromohexylmalonic ester.

d_4^{20} 0.9871; n_D^{20} 1.4376; MR_D 76.53. $C_{15}H_{28}O_5$. Calculated: MR_D 76.42.

0.2451 g substance: 0.5619 g CO_2; 0.2092 g H_2O. Found %: C 62.52; H 9.67. $C_{15}H_{28}O_5$. Calculated %: C 62.50; H 9.72.

SUMMARY

1. Sodio-malonic ester reacts with 1,5-dibromohexane to give bromohexylmalonic ester as an intermediate product.

2. The structure of the latter was confirmed by synthesis of both of the possible bromohexylmalonic esters – ε-bromohexylmalonic ester and ε-bromo-α-methylamylmalonic ester – by addition of HBr to α-methyl-δ-pentenylmalonic ester.

3. A comparison of the physical constants of both bromoesters with the properties of the bromoester obtained by the action of sodio-malonic ester on 1,5-dibromohexane, also the behavior of these substances when cyclized with the help of sodium alcoholate, show that the bromoester formed by the action of sodio-malonic ester on 1,5-dibromohexane is ε-bromohexylmalonic ester.

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SYNTHESIS OF PARTIAL ACYLALS OF LACTIC ACID

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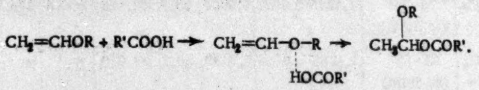
The conditions for synthesis of partial acylals from monocarboxylic acids and vinyl ethers were worked out by M. F. Shostakovsky and N. A. Gershtein [1]. Interaction of the starting components is effected without catalyst at a temperature above the boiling point of the reaction mass. This reaction is notable for its simplicity and proceeds in one step. Isolation of the products in the pure form only calls for a fractional distillation. The mechanism of formation of partial acylals by this method is represented by the equation:

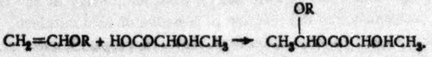


$$CH_2{=}CHOR + R'COOH \rightarrow \underset{\vdots \atop HOCOR'}{CH_2{=}CH{-}O{-}R} \rightarrow CH_3\overset{OR \atop |}{C}HOCOR'.$$

The partial acylals are obtained in a yield of 61 to 84%.

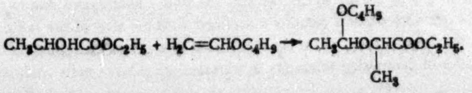
The synthesis and properties of acylals of monocarboxylic acids have been adequately studied [2-6]. Acylals of hydroxy acids, as prepared by interaction of lactic acid with vinyl ethers, have been prepared and described by us for the first time.

Lactic acid contains two functional groups and may be expected to add on vinyl ethers both at the hydroxyl and the carboxyl. However, the reaction of vinylbutyl ether with lactic acid at 25-94° showed that the products obtained are the result of addition of the acid to the ether at the carboxyl and not at the hydroxyl [7]. Consequently, the formation of alkoxy-ethylidene lactates may be represented by the equation:



$$CH_2{=}CHOR + HOCOCHOHCH_3 \rightarrow CH_3\overset{OR \atop |}{C}HOCOCHOHCH_3.$$

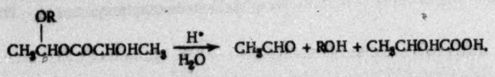
In the conditions of esterification of the carboxyl of lactic acid, another possibility is addition of the vinyl ether at the hydroxyl of this acid. Thus, when the ethyl ester of lactic acid was brought into reaction with vinylbutyl ether in an autoclave at 150-160°, a new product was formed according to the equation:



$$CH_3CHOHCOOC_2H_5 + H_2C{=}CHOC_4H_9 \rightarrow CH_3\overset{OC_4H_9 \atop |}{C}HO\underset{| \atop CH_3}{C}HCOOC_2H_5.$$

Alkoxyethylidene-lactates are soluble in alcohols, acetone, benzene and dioxane. Butoxyethylidene-lactate is less stable toward water than the corresponding butoxy-ethylidene-propionate. The lower representatives of the partial acylals of lactic acid are hydrolyzed rapidly and completely on contact with water. This behavior is evidently associated with the hydrophilic properties of lactic acid. Ethoxy- and propoxy-ethylidene-lactates are readily soluble in water and easily hydrolyzed at room temperature. With rising molecular weight the solubility in water decreases; thus, butoxy-ethylidene-lactate is only soluble in 15 times the amount of water and after energetic shaking. The optimum conditions for synthesis of partial acylals of lactic acid are a temperature of 85-100° without a catalyst in an autoclave.

The alkoxyethylidene-lactates that we prepared possess the properties common to vinyl ethers and their derivatives. Increasing molecular weight of the acylal is accompanied by a rise in boiling point and coefficient of molecular refraction and by a fall in specific gravity (see table). The yield of lactates reaches 60%. The lactic acid is partially converted into lactide, while the vinyl ether hydrolyzes to alcohol and acetaldehyde. The structure of the prepared compounds was confirmed by hydrolysis and determination of the percentage of acetaldehyde and lactic acid. The hydrolysis proceeds according to the equation



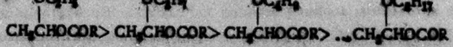
$$CH_3\overset{OR \atop |}{C}HOCOCHOHCH_3 \xrightarrow[H_2O]{H^+} CH_3CHO + ROH + CH_3CHOHCOOH.$$

Characteristics of Alkoxyethylidene-Lactates

No.	Formula	Gross formula	B.p.	n_D^{20}	d_{20}^{20}	d_4^{20}	MR_D found	MR_D calc'd	M found	M calc'd	% C found
I	$CH_3\overset{OC_4H_9}{C}HOCH(CH_3)COOC_2H_5$	$C_{11}H_{22}O_4$	105-106 (at 0.5mm)	1.4287	0.9596	0.9579	58.1	58.167	220.9	218.3	60.54
II	$CH_3\overset{OC_2H_5}{C}HOCOCHOHCH_3$	$C_7H_{14}O_4$	152-154	1.4100	1.0120	1.0102	40.0	39.498	163.4	162.2	51.65
III	$CH_3\overset{OC_3H_7}{C}HOCOCHOHCH_3$	$C_8H_{16}O_4$	166-167	1.4155	0.9835	0.9817	44.9	44.136	177.8	176.2	54.72
IV	$CH_3\overset{OC_4H_9}{C}HOCOCHOHCH_3$	$C_9H_{18}O_4$	188-189	1.4195	0.9700	0.9683	49.6	48.774	190.4	190.2	56.86
V	$CH_3\overset{OC_5H_{11}\text{-iso}}{C}HOCOCHOHCH_3$	$C_{10}H_{20}O_5$	70-74 (at 5mm)	1.4245	0.9672	0.9656	53.0	53.412	200.8	204.1	58.96
VI	$CH_3\overset{OC_6H_{13}}{C}HOCOCHOHCH_3$	$C_{11}H_{22}O_4$	81-82 (at 5mm)	1.4285	0.9656	0.9639	58.3	58.050	–	–	60.43
VII	$CH_3\overset{OC_8H_{17}}{C}HOCOCHOHCH_3$	$C_{13}H_{26}O_4$	93-96 (at 5mm)	1.4358	0.9484	0.9467	68.0	67.326	–	–	63.66
VIII	$CH_3\overset{OC_6H_{11}\text{-cyclo}}{C}HOCOCHOHCH_3$	$C_{11}H_{20}O_4$	86-88 (at 3mm)	1.4537	1.0677	1.0658	54.9	55.830	–	–	60.84

A study was later made of the interaction of lactic acid with isoamyl-, hexyl-, octyl- and cyclohexylvinyl ethers. Synthesis of lactates (V, VI, VII, and VIII) was accomplished without a catalyst under the influence of heat (85-100°), both at normal pressure and in an autoclave. The yield of products was 5 to 27%. The low yield of lactates is bound up with the properties of the vinyl ethers which react slowly and far from completely at 85-100°. On the other hand, rise of temperature to above 100° or performance of the reaction in presence of acid catalysts, leads to resinification and lowers the yield of lactates. The prepared lactates differ from the lower representatives of the series (I, II, III and IV) in being insoluble in water. Their hydrolysis proceeds under the influence of water, acids or alkalies at 100° and on prolonged heating in sealed ampoules; this process was utilized for establishing the structure of the lactates.

The described compounds are readily soluble in ethyl ether and acetone, less soluble in benzene and dioxane. After keeping for a long period (up to 3 months) the lactates are slowly hydrolyzed due to the action of atmospheric moisture. The slowness of water absorption is possibly correlated with the size of the radical (isoamyl, hexyl, octyl, cyclohexyl) which protects the free hydroxyl of lactic acid and makes it less hydrophilic. The partial acylals may be arranged in the following order of decreasing solubility in water:



$$CH_3\overset{OC_2H_5}{C}HOCOR > CH_3\overset{OC_3H_7}{C}HOCOR > CH_3\overset{OC_4H_9}{C}HOCOR > \ldots CH_3\overset{OC_8H_{17}}{C}HOCOR$$

Whereas the first two members of the series have good solubility in water, butoxyethylidene-lactate is only soluble in 15 times its volume of water, while isoamyloxyethylidene-lactate and the higher members of the series are insoluble in water.

EXPERIMENTAL

1. Interaction of Ethyl Lactate with Vinylbutyl Ether

59 g ethyl lactate (b.p. 153-155°; n_D^{20} 1.4013; d_4^{20} 1.0310) and 50 g vinylbutyl ether (b.p. 93-94°; n_D^{20} 1.4025; d_4^{20} 0.7793) were heated in an autoclave for 8 hours at 150-160°. 102 g of a yellow liquid was discharged and on fractionation gave a substance with b.p. 102-106° (0.5 mm); n_D^{20} 1.4186; resinous residue 9.7 g; weight of material in trap 23.9 g.

The contents of the trap were treated with metallic sodium and then distilled at 145-147°; n_D^{20} 1.3990; d_{20}^{20} 0.8312; d_4^{20} 0.8297. The constants agree with those for acetaldehyde-ethylbutyl acetal. The ethyl alcohol for reaction

%C calc'd	%H found	%H calc'd
60.53	10.06	10.16
51.85	8.43	8.64
54.53	9.12	9.15
56.84	9.67	9.47
58.84	9.72	9.81
60.52	10.17	10.16
63.38	10.82	10.64
61.08	9.48	9.32

with vinylbutyl ether is probably formed by decomposition of the ethyl lactate. The yield of acetaldehyde-ethylbutyl acetal was 18.26 g (25% on the vinylbutyl ether).

0.1399 g substance: 18.27 g benzene: Δt 0.267°. 0.2575 g substance: 18.27 g benzene: Δt 0.495°. Found: M 146.26, 145.21. $C_8H_{18}O_2$. Calculated: M 146.224. 0.1005 g substance: 25 ml bisulfite: 17.7 ml 0.1 N I_2. 0.1153 g substance: 25 ml bisulfite: 15.4 ml 0.1 N I_2. For 25 ml bisulfite, 30.4 ml 0.1 N I_2 was consumed. Found %: acetal 91.89, 95.12.

The substance with b.p. 102-106° (0.5 mm) was carefully treated with metallic calcium and distilled; it was identified as butoxyethylidene-2-lacto-3-ethylate whose formula (I) and main constants are given in the table. Yield 63.6 g (58.3% of the theoretical).

Hydrolysis with determination of the percentage of acylal as acetaldehyde: 0.1207 g substance: 25 ml bisulfite: 19.7 ml 0.1 N I_2. 0.1299 g substance: 25 ml bisulfite: 19.0 ml 0.1 N I_2. For 25 ml bisulfite was consumed 30.7 ml ml 0.1 N I_2. Found %: acylal 95.32, 97.53.

Hydrolysis with alcoholic KOH with determination of the percentage of acylal as acid: 0.2817 g substance: 13.0 ml 0.1 N HCl. 0.3015 g substance: 13.9 ml 0.1 N HCl. Found %: acylal 100.8, 100.7.

2. Interaction of Lactic Acid with Vinylethyl Ether

90 g lactic acid, previously purified through the magnesium salt [8], with m.p. 17-18° and b.p. 118-119° (12 mm), and 72 g vinylethyl ether (b.p. 36-36.5°; n_D^{20} 1.3780; d_4^{20} 0.7530, were charged into a flask cooled with tap water. After adding 0.1-0.2 g P_2O_5, the mixture froths violently and resinifies, the temperature rising to 42-45°. On lowering the temperature in the flask to 35°, this temperature is maintained for 1-1½ hours with a warm water bath. Over night the mixture in the flask separates into two layers: the upper one liquid, the lower one viscous (107 g and 50 g respectively). This viscous product had b.p. 118-119° (12 mm). Titration with alkali indicated that it was a monobasic acid.

0.2210 g substance: 24.5 ml 0.1 N NaOH. Found %: acid 99.88. Lactic acid recovered 45.2 g (50%).

Fractionation of the liquid gave: 1) b.p. 35-36°, n_D^{20} 1.3772 — 40 g; 2) b.p. 148-154°, n_D^{20} 1.4098 — 55 g; resinous residue 8 g.

The first fraction, after washing with water and drying, distilled at 36-36.5°; n_D^{20} 1.3780; d_4^{20} 0.7523. The constants agree with those of vinylethyl ether. Recovered from the reaction 36.1 g (50%).

0.0587 g substance: 25 ml bisulfite; 15.1 ml 0.1 N I_2. 0.0769 g substance: 25 ml bisulfite: 10.1 ml 0.1 N I_2. For 25 ml bisulfite was consumed 30.1 ml 0.1 N I_2. Found %: ether 92.13, 93.76.

The second fraction, after careful treatment with a small amount of metallic calcium, distilled at 152-154° and consisted of ethoxyethylidene-lactate whose formula (II), constants and analysis are given in the table. Yield 52 g (32% of the theory).

Hydrolysis with determination of the percentage of acylal as acetaldehyde: 0.1168 g substance: 25 ml bisulfite: 16.7 ml 0.1 N I_2. 0.1264 g substance: 25 ml bisulfite: 15.4 ml 0.1 N I_2. For 25 ml bisulfite was consumed 30.7 ml 0.1 N I_2. Found %: acylal 97.20, 96.15.

Hydrolysis with determination of the percentage of acylal as acid: 0.2893 g substance: 18.0 ml 0.1 N HCl. 0.2368 g substance: 14.9 ml 0.1 N HCl. Found %: acylal 100.9, 101.98.

3. Synthesis of Ethoxyethylidene-Lactate (II) in the Autoclave

A mixture comprising 90 g lactic acid and 72 g vinylethyl ether was heated in an autoclave for 6 hours at 85-90°. 150 g yellow product was discharged and separated into two layers. From the upper liquid layer was isolated 27.4 g (38%) vinylethyl ether with b.p. 36-36.5°; n_D^{20} 1.3780, and 84.3 g (52%) ethoxyethylidene-lactate with b.p. 152-154°; n_D^{20} 1.4100. The viscous lower layer was vacuum-distilled to give: 1) 28.9 g (32%) with b.p. 117-119° (12 mm); 2) 6 g with b.p. 138-142° (8 mm), crystallizing at room temperature.

The first fraction, lactic acid, was identified by titration with alkali in presence of phenolphthalein.

0.2815 g substance: 31.4 ml 0.1 N NaOH; 0.2017 g substance: 22.6 ml 0.1 N NaOH. Found %: lactic acid 100.48, 100.9.

The second fraction, after 3 recrystallizations from ethyl alcohol, melted at 124°. The acicular crystals were moderately soluble in ethyl alcohol and ether. The data identify the substance as the D, L-lactide of lactic acid. Yield 4 g (5.5%). Literature data [8]: b.p. 142° at 8 mm, m.p. 124.5°.

7.283 mg substance: 13.342 mg CO_2; 3.700 mg H_2O. 5.635 mg substance: 10.320 mg CO_2 2.175 mg H_2O. Found %: C 49.99, 49.98; H 5.68, 5.51. $C_6H_8O_4$. Calculated %: C 50.00; H 5.56.

4. Interaction of Lactic Acid with Vinylpropyl Ether

The synthesis of propyxyethylidene-lactate (III) and the treatment of the reaction products were effected in the conditions of experiment 3. From 90 g lactic acid and 86 g vinylpropyl ether were obtained: propoxyethylidene-lactate 89.4 g (50.8%), vinylpropyl ether 34.5 g (40%) and lactic acid 30 g (33%).

5. Interaction of Lactic Acid with Vinylbutyl Ether

90 g lactic acid and 100 g vinylbutyl ether were charged into a flask. After introduction into the mixture of 0.1-0.2 g P_2O_5, the temperature was raised to 80-95° for 20 minutes while cooling with tap water. The mixture was then heated for 2 hours at 90°. 185 g was discharged. Fractionation gave: 1) 90-94°; n_D^{20} 1.4023 — 5.5 g; 2) b.p. 187-191°; n_D^{20} 1.4200 — 80 g; 3) b.p. 120-122° (14 mm); n_D^{20} 1.4415 — 41.5 g; 4) b.p. 138° (7 mm), 6 g; the substance crystallized.

After washing with water and drying, the first fraction distilled at 93-94°; n_D^{20} 1.4028; d_4^{20} 0.7794. The data correspond to those for vinylbutyl ether. Recovered from the reaction 51 g (51%).

0.1009 g substance: 25 ml bisulfite; 10.4 ml 0.1 N I_2. 0.1202 g substance: 25 ml bisulfite; 7.4 ml 0.1 N I_2. For 25 ml bisulfite 30.4 ml 0.1 N I_2 was consumed. Found % ether: 99.26, 95.82.

The second fraction, after careful treatment with a little metallic calcium, distilled at 188-189° and was butoxyethylidene-lactate; its formula, constants and analysis are given in the table. Yield 76 g (40% of the theoretical)

Hydrolysis with determination of the acylal as acetaldehyde: 0.2003 g substance: 25 ml bisulfite; 10.2 ml 0.1 N I_2. 0.2019 g substance: 25 ml bisulfite; 10.0 ml 0.1 N I_2. For 25 ml bisulfite 30.3 ml 0.1 N I_2 was consumed. Found %: acetal 95.45, 95.66.

Hydrolysis with determination of percentage of acylal as acid: 0.1938 g substance: 10.2 ml 0.1 N HCl. 0.2015 g substance: 10.7 ml 0.1 N HCl. Found %: acylal 100.7, 101.04.

The third fraction was identified as lactic acid; the amount recovered was 41.5 g (46%). 0.2138 g substance: 23.8 ml 0.1 N NaOH. Found %: acid 100.38.

The fourth fraction, after recrystallization from ethyl alcohol, melted at 123-124°, in agreement with the m.p. of D,L-lactide [8]. Yield 4.8 g (6.6%).

6. Synthesis of Butoxyethylidene-lactate (IV) in an Autoclave

A mixture of 90 g lactic acid and 100 g vinylbutyl ether was heated for 6 hours at 85-95° in an autoclave. The mixture was worked up to give the following products: vinylbutyl ether 40.3 g (40%), b.p. 93-94°, n_D^{20} 1.4026; butoxyethylidenelactate 100.3 g (52.8%), b.p. 188-189°, n_D^{20} 1.4195; d_4^{20} 0.9684; lactic acid 32 g (35.5%), b.p. 120-122° (14 mm); D,L-lactide 4.4 g (6.1%), m.p. 124°.

7. Interaction of Lactic Acid with Vinylisoamyl Ether

The synthesis of isoamyloxyethylidene-lactate (V) and the working-up of the reaction products were performed in the conditions of experiment 3. From 90 g lactic acid and 114 g vinylisoamyl ether (b.p. 112°, n_D^{20} 1.4098) was obtained: 55.9 g (27.4%) isoamyloxyethylidene-lactate, 61 g (68%) lactic acid and 74 g (65%) vinylisoamyl ether.

8. Preparation of Hexyloxyethylidene-lactate

A mixture of 83.2 g vinylhexyl ether (b.p. 143.5°; n_D^{20} 1.4171; d_4^{20} 0.7970) and 60.5 g lactic acid (b.p. 121-122° at 14 mm) was heated for 10 hours in an autoclave at 85-95°. 134.6 g was discharged. Fractionation gave:

first fraction 54.7 g, b.p. 55-60° (8 mm), n_D^{20} 1.4145; second fraction 39.3 g, b.p. 91-142° (8 mm), n_D^{20} 1.4288. The viscous residue in the flask (49.7 g) was not investigated. After the first fraction had been treated with metallic sodium, it distilled at 143.5°, n_D^{20} 1.4170, d_4^{20} 0.7969, which corresponds to vinylhexyl ether.

The constants of the second fraction, after repeated distillation, corresponded to hexyloxyethylidene-lactate (VI). Yield 16.65 g or 11.6% of the theoretical.

Hydrolysis with determination of the percentage of acylal as acid: 0.7000 g substance: 32.5 ml 0.1 N HCl, 0.5700 g substance: 26.4 ml 0.1 N HCl. Found %: acylal 101.03, 101.11.

9. Preparation of Octyloxyethylidene-lactate

A mixture of 156 g vinyloctyl ether (b.p. 186-187°, n_D^{20} 1.4274, d_4^{20} 0.8028), and 90 g lactic acid was charged into a three-necked flask fitted with a mechanical stirrer, mercury seal and reflux condenser, and connected to a trap and a thermometer which reached to the bottom of the flask; the mixture was heated for 13 hours at 85-99° and acquired a dark-brown color; on standing it separated into two layers. The upper layer (liquid) was filtered off from the precipitate – lactic acid. The amount of lactic acid recovered was 80 g (90%). Distillation of the filtrate in a current of dry nitrogen gave: first fraction, 60 g, b.p. 50-104° (5 mm), n_D^{20} 1.4280; second fraction, 19.5 g, b.p. 105-109° (5 mm), n_D^{20} 1.4323; third fraction, 18.9 g, b.p. 110-132° (5 mm), n_D^{20} 1.4325; fourth fraction, 39.0 g, b.p. 133-143° (5 mm), n_D^{20} 1.4365.

After treatment with metallic sodium the first fraction was distilled at normal pressure: b.p. 185-187°; n_D^{20} 1.4275. The substance is identical with vinyloctyl ether. Amount recovered 52.5 g (33%).

Fractions 2, 3 and 4 were combined. Repeated vacuum distillation in a current of dry nitrogen gave 12.6 g (5.1%) octyloxyethylidene-lactate (VII), whose constants are given in the table.

Hydrolysis with determination of the percentage of acylal as acid: 0.6532 g substance: 26.7 ml 0.1 N HCl. 0.7586 g substance: 30.9 ml 0.1 N HCl. Found %: acylal 100.6, 100.4

10. Preparation of Cyclohexyloxyethylidene-lactate

A mixture of 126 g vinylcyclohexyl ether (b.p. 147-148°, n_D^{20} 1.4546) and 90 g lactic acid was heated for 7 hours to 75-90° (different from the conditions in experiment 9). The reaction mixture was worked up to give: 11.5 g (5.3%) cyclohexyloxyethylidene lactate (VIII), 107 g vinylcyclohexyl ether (85%) and 80 g (89%) lactic acid.

SUMMARY

A description is given for the first time of the interaction of ethyl lactate with vinylbutyl ether and of the interaction of lactic acid with the following vinyl ethers: ethyl, propyl, butyl, isoamyl, hexyl, octyl and cyclohexyl.

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* See Consultants Bureau Translation, p. 1581.

THE REACTION BETWEEN ISOPROPYLMAGNESIUM CHLORIDE AND METHYL CHLOROFORMATE

G. A. Razuvaev and Yu. A. Oldekop

The reactions of esters of chloroformic acid with RMgX have been little studied in the past. V. K. Matsurevich [1] prepared triethylcarbinol and tripropylcarbinol from chloroformic ester and the appropriate RMgX. Zh. I. Iotsich [2] prepared the unsaturated alcohol, triallylenecarbinol, by reaction between chloroformic ester and allylenemagnesium bromide. Thus, the reaction between alkylmagnesium halides and an ester of chloroformic acid usually gives the corresponding tertiary alcohol.

In the investigation of several syntheses with RMgX it was shown that in the case of branched radicals, for example isopropyl, tert.-butyl and certain others, the main reaction of formation of tertiary alcohol is accompanied by another reaction involving reduction of the carbonyl compound. In some cases the normal formation of the corresponding tertiary alcohol is completely overshadowed by the reduction reaction [3]. This form of the reaction has been mainly studied with aldehydes, ketones and esters. As far as we know, transformations of this type have not been studied with chloroformic esters.

We have investigated the reaction between isopropylmagnesium chloride and methyl chloroformate. The components were in the ratio of 1 mole isopropylmagnesium chloride to 0.3 mole ester, i.e., the ratio most favorable to the formation of a tertiary alcohol.

The main products isolated from the reaction mixture, however, were diisopropylcarbinol and methyl isobutyrate. The tertiary alcohol – triisopropylcarbinol – could not be isolated. Consequently the main direction of the reaction is a reduction. The most probable mechanism of the reaction is that of Houben: formation of methyl isobutyrate as an intermediate which reacts with isopropylmagnesium chloride to form diisopropyl ketone, and the latter is reduced to diisopropylcarbinol in the reaction conditions.

We confirmed the formation of diisopropyl ketone from methyl isobutyrate and isopropylmagnesium chloride by a specially designed experiment.

EXPERIMENTAL*

Reaction of methyl chloroformate with isopropylmagnesium chloride. To the organomagnesium compound prepared from 24 g magnesium and 78.5 g (1.0 mole) isopropyl chloride was added dropwise, with cooling, over a period of 1 hour 28.5 g (0.3 mole) methyl chloroformate.

The reaction mixture was left for 2 hours, after which it was decomposed with dilute hydrochloric acid (1:10). The ether layer was washed with 10% sodium carbonate solution and dried over anhydrous sodium sulfate. After the ether had been driven off, the residue of 33 g was fractionated in a Vigreux column (35 cm long).

Fractions: 40-78°, 9.2 g; 79-93° 5.6 g; 94-134°, 0.9 g; 135-141°, 3.9 g; 142-182°, 1.2 g; 182-186°, 3.1 g, residue, 2.7 g.

For analytical purposes the following fractions were obtained by a second distillation: I 89-94°; II 137-141°, III 183-186°.

The first fraction with b.p. 89-94° consisted of methyl isobutyrate. No active hydrogen was found. Saponification gave isobutyric acid; m.p. of its anilide 98° (literature: 105°). The N-benzylamide of isobutyric acid was also prepared with m.p. 86.4°; it did not depress the melting point in admixture with an authentic specimen of the benzylamide of isobutyric acid. The yield of methyl isobutyrate, calculated on the methyl chloroformate taken, is 18.2%.

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* Z. N. Zudina and Yu. A. Sorokin participated in the experimental work.

The second fraction with b.p. 137-141° consisted of diisopropylcarbinol.

d_4^{20} 0.8302, n_D^{20} 1.418; MR_D 35.3, calculated 36.1.

Found %: OH 14.1, 13.8; M 115.2, 115.7. $C_7H_{16}O$. Calculated %: OH 14.6; M 116.

Found %: C 71.5; H 14.0. $C_7H_{16}O$. Calculated %: C 72.3; H 13.7.

The substance was benzoylated by the Schotten-Baumann reaction and subjected to combustion.

Found %: C 75.8; H 9.4. $C_{14}H_{20}O_2$. Calculated %: C 76.3; H 9.1.

The yield of diisopropylcarbinol, calculated on the methyl chloroformate taken, was 28.3%.

Third fraction with b.p. 183-186°; d_4^{20} 0.8965; n_D^{20} 1.424. Found %: OH 7.5. This fraction was not further investigated.

Reaction between methyl isobutyrate and isopropylmagnesium chloride. The organomagnesium synthesis in the usual conditions with 5.6 g magnesium, 18 g isopropyl chloride and 10 g methyl isobutyrate gave a liquid from which diisopropyl ketone could be isolated. Preparation was carried out of the 2,4 dinitrophenylhydrazone with m.p. 95° and of the semicarbazone with m.p. 160°, in agreement with the literature data for these derivatives.

SUMMARY

1. Among the products of reaction of isopropylmagnesium chloride with methyl chloroformate were found diisopropylcarbinol and methyl isobutyrate. A tertiary alcohol could not be detected.

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INTERACTION OF SUBSTANCES CONTAINING ACTIVE METHYLENE GROUPS WITH DIAZO COMPOUNDS

A. A. Kharkharov

In organic chemistry a large number of compounds are encountered which are characterized, in comparison with saturated hydrocarbons, by very high lability of the methyl groups.

These compounds condense with carbonyl compounds (aldehydes and ketones), esters and anhydrides of carboxylic acids, and nitroso compounds; they also exchange the hydrogen of their methyl groups for deuterium and alkali metals [1-14].

We established for the first time that some members of this type of compounds are also capable of coupling with aromatic diazo compounds with formation of unusual azo dyes [15-19]

$$R{-}CH_3 + XN_2R_1 \rightarrow R_1{-}CH_2{-}N{=}N{-}R_1 + HX$$

or

$$R{-}CH_3 + XN_2R_1 \rightarrow R{-}CH{=}N{-}NH{-}R_1 + HX$$

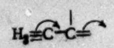
This reaction was found to necessitate a higher activity of the methyl group than is required for condensation with carbonyl and nitroso compounds [16].

It was established that the requisite mobility of the hydrogens of the methyl group may be guaranteed by directly linking it with heterocyclic residues or with residues of aromatic compounds containing electrophilic substituents in the ortho and para- positions to the methyl group [15-19]. In the latter case the requisite activity of the methyl group is only achieved by introducing into the molecule several substituents with greater attractive power for electrons.

Thus, toluene and its derivatives containing nucleophilic substituents (for example xylenes) do not react with diazo compounds through the methyl group. Also incapable of undergoing this reaction are derivatives of toluene containing weak electrophilic groups: $-SO_3H$, $-COOH$, $-COR$ [19, 20]. It was found that only three nitro groups in the ortho- and para- positions impart to toluene the ability to couple with diazo compounds [19]. All other electrophilic substituents exert an inadequate effect.

From what has been said it follows that electrophilic substituents which increase the lability of the hydrogens of the methyl group can only endow these compounds with the ability to undergo azo coupling if they are conjugated with the methyl group and if they possess a sufficiently strong attractive power for the electrons of other atoms.

The increased lability of the hydrogen atoms of methyl groups due to redistribution of the electronic densities in the conjugated system under the influence of electrophilic atoms or groups is represented as follows:



We have shown that nucleophilic groups, in contrast to electrophilic groups, lower the lability of the hydrogens of methyl groups. Thus, the introduction into 2,4,6-trinitrotoluene of one more methyl group deprives it of the ability to react with diazo compounds [19].

In work with methylpyridines and methylacridines we established that the α- and γ-derivatives of some heterocyclic compounds are so active that they are capable of azo-coupling even in the absence of electrophilic substituents [15-18].

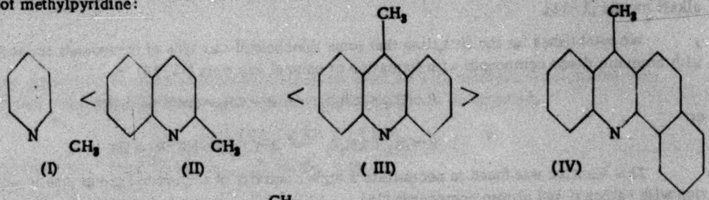
It was subsequently shown that this was also the case with benzo derivatives of methylacridine [22] and with methylpyrimidines [23].

The activity of unsubstituted 9-methylacridine toward diazo compounds is considerably higher than that of 2,4,6-trinitrotoluene. Whereas the latter compound does not couple even with such highly reactive compounds as p-sulfodiazobenzene, 9-methylacridine readily reacts not only with p-sulfodiazobenzene but also with weakly active diazo compounds containing several nucleophilic substituents, for example with 2,5-dimethoxy-4-phenylaminodiazobenzene.

The explanation of this phenomenon (on the basis of the scheme presented above) must be sought in the fact that the nitrogen of the heterocycle conjugated with the methyl group tends to increase its electronic density at the expense of both the inductive effect (according to its position in the Mendeleev system) and the conjugation effect. In other words, the heteroatom functions as a very strong electrophilic substituent. To this it is only necessary to add that the lability of the hydrogen atoms of the methyl groups is strongly influenced by the interaction of the three pairs of π-electrons of the benzene rings as well as, in particular, of the hetero rings.

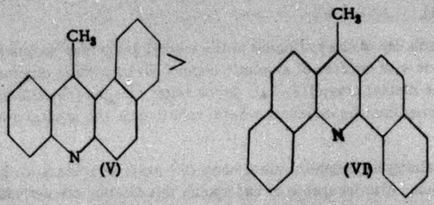
The adduced experimental data are fully consistent with the theory—extensively developed by A. N. Nesmeyanov [21]—of the conjugation of the σ-electrons (σ-conjugation), and they must be regarded as a particular case of this phenomenon.

The effect of condensed aromatic rings on the activity of methyl groups may be illustrated with reference to benzo derivatives of methylpyridine:



(I) (II) (III) (IV)

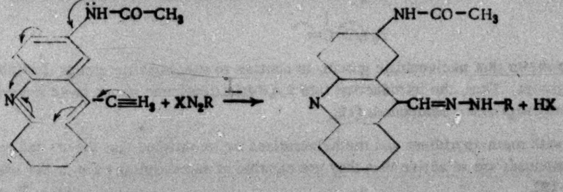
and



(V) (VI)

The successive increase in the mobility of the hydrogen in compound (II) and especially in compound (III) in comparison with (I) is due to supplementary interaction of the electrons of the methyl groups with the benzene rings. The fall in this mobility on passage from (III) to (VI) [22] is evidently due to the naphthalene nuclei possessing a less pronounced aromatic character and, consequently a weaker electrophilic character than the benzene rings. Hence, the attraction of the σ-electrons will be the weaker the larger the number of naphthalene nuclei in the compound.

This research also shows that in contrast to 2,4,6-trinitrotoluene, where the introduction of only one weakly nucleophilic substituent (a methyl group) deprives it of the ability to undergo azo coupling, the introduction in the 2-position to the acridine nitrogen of 9-methylacridine of the acetylamino group (much more strongly electron-repelling) does not deprive it of the ability to interact with diazo compounds:



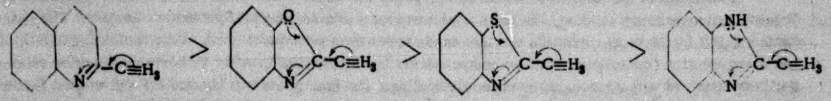
It was found, however, that also in this case the introduction of a nucleophilic substituent into the molecule lowers the reactivity of the methyl group.

Whereas 9-methylacridine readily couples with nearly all aromatic diazo compounds, 2-acetylamino-9-methylacridine interacts only with the most active of these. It reacts slowly with phenyldiazonium, rather more quickly with p-nitrophenyldiazonium, and does not react at all with p-methoxyphenyldiazonium.

From what has been said it follows that the heterocyclic nitrogen atom located in the α and γ-positions to the methyl group is so strongly activated by the latter that the compound retains the ability to couple even when the activating action of the heteroatom is reduced by the introduction of nucleophilic groups into its molecule.

The arylhydrazones of 2-acetylamino-9-acridine aldehyde that we prepared by the diazo reaction differ from the corresponding arylhydrazones of 9-acridine aldehyde by the position of their main absorption bands which are in the short-wave region of the spectrum (Fig. 1).

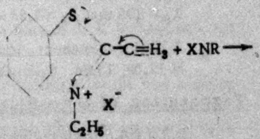
Previously, we had shown [16] that heterocyclic compounds of the type of quinaldine, 2-methylbenzoxazole, 2-methylbenzothiazole and 2-methylbenzimidazole may be arranged in the following order in respect of the activity of their methyl groups:

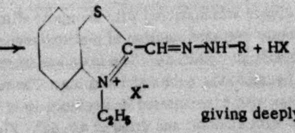


The fact that the head of this series is 2-methylbenzimidazole may be accounted for by the nitrogen atom of the $-\ddot{N}H-$ group, by virtue of its position in the periodic system of the elements, tending more strongly than the $-\ddot{S}-$ atom and the $-\ddot{O}-$ atom to reduce its electronic density at the expense of the conjugative effect with the α-carbon, so that the ionization tendency of the hydrogen is reduced. The transition of these compounds into the onium state, however, leads to heightened activity of their methyl groups [16].

In this investigation we illustrate this thesis by reference to the previously uninvestigated interaction of 2-methylbenzothiazole ethoiodide with diazo compounds.

Unlike methylbenzylimidazole and methylbenzothiazole, which are incapable of coupling, the ethoiodide derivative of the latter readily enters into reaction with diazo compounds:





giving deeply colored dyes (Fig. 2).

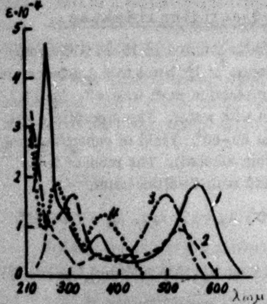


Fig. 1. Curves of absorption spectra. 1 - 9-acridine aldehyde phenylhydrazone; 2 - 9-acridine aldehyde p-nitrophenylhydrazone; 3 - 2-acetylamino-9-acridine aldehyde phenylhydrazone; 4 - 2-acetylamino-9-acridine aldehyde p-nitrophenylhydrazone (all in 0.2 N alcoholic HCl).

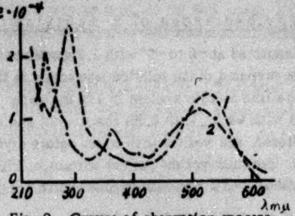


Fig. 2. Curves of absorption spectra. 1 - Cation of 1-ethyl-4'-nitrophenyl-2-benzothiazolealdehyde; 2 - cation of 10-ethyl-4-nitrophenylhydrazone of 9-acridinealdehyde (both in alcohol).

EXPERIMENTAL

Preparation of 2',5'-Dimethoxy-4-phenylaminophenylhydrazone of 9-Acridinealdehyde

1.4 g 2,5-dimethoxy-4-aminodiphenylamine was diazotized at −5° with 0.4 g sodium nitrite in a solution of 6 ml water and 2ml 37% hydrochloric acid. The filtered diazo solution was added dropwise in the course of an hour to 18 g 9-methyl-acridine and 5 g crystalline sodium acetate dissolved in 24 ml 80% acetic acid. The reaction mass was kept at room temperature for 40 hours; it was then diluted with 60 ml water and filtered from the precipitate. The latter was washed with water, with 0.5% acetic acid and again with water; it was then treated with 5% ammonia, thoroughly washed with water and dried at 70–80°. Yield of unpurified product 2.2 g (43% of the theoretical).

After recrystallization from a mixture of alcohol and pyridine, the product had m.p. 141°. The dark-red powder is insoluble in water, soluble in alcohol (brown solution) and in acetic acid (greenish-blue coloration).

Maxima of absorption bands in 0.2 N alcoholic HCl: $\lambda_1 = 258$ mμ, $\epsilon_1 = 5.12 \cdot 10^4$; $\lambda_2 = 360$ mμ, $\epsilon_2 = 1.68 \cdot 10^4$; $\lambda_3 = 630$ mμ, $\epsilon_3 = 1.9 \cdot 10^4$.

0.1225 g substance: 13.3 ml N_2 (21°, 760 mm). Found %: N 12.60. $C_{28}H_{24}O_2N_4$. Calculated %: N 12.50.

Preparation of the Phenylhydrazone of 2-Acetylamino-9-acridinealdehyde

2.35 g freshly distilled aniline was diazotized at 0° with 1.8 g sodium nitrite in a solution of 17 ml water and 12.5 ml 37% hydrochloric acid.

Two-thirds of the solution of the diazo compound was added over a period of 6 hours to a solution of 6.3 g 2-acetylamino-9-methylacridine, 150 ml glacial acetic acid and 20 g crystalline sodium acetate. The reaction mass was left for 20 hours. Addition was then made to it over a period of 2 hours of the remaining one-third of the diazo solution (the solution of diazo compound was freshly prepared). After 24 hours the reaction mixture was partly neutralized with aqueous ammonia while cooling. The precipitate was filtered off and washed first with water, then with 0.5% acetic acid and again with water; it was then treated with 5% ammonia solution, washed with water and dried at 50–60°. Yield of unpurified product 5.8 g (65.9% of the theoretical).

The dark-brown powder (from ethyl alcohol) had m.p. 111°. The product is insoluble in water; it dissolves in alcohol with a brownish-yellow, and in glacial acetic acid with a brownish-red color.

Absorption maxima in 0.2 N alcohol HCl: $\lambda_1 = 314$ mμ, $\epsilon_1 = 1.64 \cdot 10^4$; $\lambda_2 = 512$ mμ, $\epsilon_2 = 1.64 \cdot 10^4$.

0.1278 g substance: 16.7 ml N_2 (18°, 766 mm). Found %: N 15.41. $C_{22}H_{18}ON_4$. Calculated %: N 15.82.

Preparation of p-Nitrophenylhydrazone of 2-Acetylamino-9-acridinealdehyde

3.5 g p-nitroaniline was diazotized at –5 to –7° with 1.8 g sodium nitrite in solution in 15 ml 37% hydrochloric acid and 28 ml water. The prepared diazo solution was added in the course of 1½ hours to 6.3 g 2-acetylamino-9-methylacridine, 25 g crystalline sodium acetate in 100 ml water. The reaction mass was left for 17 hours. The precipitate was washed with water, with 0.5% acetic acid and again with water. The precipitate was then treated with 5% ammonia, filtered, and washed with water before drying at 50–60°. Yield of unpurified product 5.5 g (55% of the theoretical). Brownish-yellow powder with m.p. 178° (from alcohol). The product is insoluble in water; it dissolves in alcohol with a brownish-yellow and in acetic acid with a yellow color.

Absorption maxima in 0.2 N alcoholic HCl: $\lambda_1 = 222$ mμ, $\epsilon_1 = 3.0 \cdot 10^4$; $\lambda_2 = 278$ mμ, $\epsilon_2 = 1.84 \cdot 10^4$; $\lambda_3 = 375$ mμ, $\epsilon_3 = 1.24 \cdot 10^4$.

0.1004 g substance: 14.5 ml N_2 (17°, 764 mm). 0.1210 g substance: 18 ml N_2 (15°, 758 mm). Found %: N 17.08, 17.64. $C_{22}H_{17}O_3N_5$. Calculated %: N 17.54.

Preparation of ω-(o-Nitrobenzeneazo)-2,4,6-trinitrotoluene

2.3 g 2,4,6-trinitrotoluene was dissolved with energetic stirring in 50 ml pyridine, and to the red solution was added dropwise a previously prepared solution of p-nitrodiazobenzene (from 1.38 g p-nitroaniline), partly neutralized beforehand with sodium carbonate. The mass was stirred for 16 hours, after which it was poured onto a mixture of 45 ml 37% hydrochloric acid and 100 g ice. The resultant brown mass was filtered; the precipitate was triturated in a mortar with concentrated hydrochloric acid; the suspension was filtered; the precipitate was washed with water, then with alcohol, and dried at 40–60°. Yield of unpurified product 4.1 g (88% of the theoretical). After purification by elimination of starting materials with alcohol and recrystallization from glacial acetic acid, the melting point rose to 177°.

The water-insoluble brownish-red powder dissolved in 95% sulfuric acid with a violet coloration (λ_{max} ~550 mμ). When the sulfuric acid solution was diluted with water, the product separated in the form of red flocs. It is soluble in alcohol, ether, acetone and glacial acetic acid; insoluble in gasoline and carbon tetrachloride.

0.0853 g substance: 16.4 ml N_2 (18°, 764 mm). Found %: N 22.51. $C_{13}H_8O_8N_6$. Calculated %: N 22.34.

Product of Coupling of α-Methylimidazole with Diazotized p-Nitroaniline

To a solution of 1 g α-methylimidazole and 10 g sodium acetate in 50 ml acetic acid was added over a period of 2 hours a previously prepared solution of the diazo compound from 1.38 g p-nitroaniline. The reaction mass was kept from 20 hours. The dark-brown precipitate was filtered off, washed with water, treated with dilute ammonia, washed with water and dried at 50-60°. Yield of unpurified product (m.p. 120°), 1.48 g (64% of the theoretical. After recrystallization from alcohol the m.p. was 129°.

The brown powder had m.p. 129-130° after recrystallization from methyl alcohol. The product does not dissolve in water; it dissolves in alcohol and acetic acid with a brownish-yellow color. Maxima of absorption bands: $\lambda_1 = 280$ mμ, $\epsilon_1 = 2.75 \cdot 10^4$; $\lambda_2 = 390$ mμ, $\epsilon_2 = 2.2 \cdot 10^4$.

0.0878 g substance: 23.2 ml N_2 (22°, 758 mm). Found %: N 30.49. $C_{10}H_9O_2N_5$. Calculated %: N 30.30.

Preparation of ω-(p-Nitrobenzeneazo)-α-methylpyridine

1.38 g p-nitroaniline was diazotized with 0.7 g sodium nitrite in solution in 6 ml hydrochloric acid and 11 ml water. Over a period of 1 hour the diazo solution was added to a mixture of 1.5 g α-methylpyridine with b.p. 129-130°, 50 ml 80% acetic acid and 10 g crystalline sodium acetate. After standing for 30 hours, the precipitate was filtered off, washed with water, then with 5% ammonia and finally with water before drying at 45-50°. Yield of unpurified product 1.4 g (58% of the theoretical). Yellow powder with m.p. 92° (from methyl alcohol). The product is soluble in alcohol and acetic acid; insoluble in water.

0.1086 g substance: 22.1 ml N_2 (22°, 756 mm). Found %: N 23.42. $C_{12}H_{10}O_2N_4$. Calculated %: N 23.14.

Preparation of ω-(p-nitrobenzeneazo)-3,5-dicarboxy-2,6-dimethylpyridine

1.38 g p-nitroaniline was diazotized with 0.7 g sodium nitrite in a solution of 6 ml 37% hydrochloric acid and 11 ml water. The resultant diazo solution was added over a period of 1 hour to a mixture of 2.4 g of the disodium salt of 2,6-dimethylpyridine-3,5-dicarboxylic acid, 40 ml 80% acetic acid and 10 g crystalline sodium acetate. After 20 hours' standing, the precipitate was filtered off, washed with water and dried at 50-60°. Yield of unpurified product 3.25 g (94% of the theoretical).

The yellowish-brown, water-insoluble powder is soluble in alcohol with a brownish-yellow color and in acetic acid with a yellow color. After purification with the help of acetic acid, the product had m.p. 174°. Maxima of the absorption bands of the alcoholic solutions: $\lambda_1 = 280$ mμ, $\epsilon_1 = 1.91 \cdot 10^4$; $\lambda_2 = 400$ mμ, $\epsilon_2 = 1.52 \cdot 10^4$.

0.1085 g substance: 15.1 ml N_2 (23°, 763 mm). Found %: N 16.10. $C_{15}H_{12}O_6N_4$. Calculated %: N 16.28.

SUMMARY

1. Azo-coupling at the methyl group was a logical development of the earlier work of A. E. Porai-Koshits on the lability of the hydrogen atoms of organic compounds.

2. It was established that the lability of the hydrogens of the methyl group necessary for the azo-coupling reaction can be secured by direct linkage to the methyl group of heterocyclic residues or of residues of aromatic compounds containing electrophilic substituents in the ortho- and para- positions to the methyl group (σ-conjugation).

3. It was shown that residues of pyridine, quinoline, acridine, benzoacridines and dibenzoacridines and other similar heterocycles, connected through the α- and σ-positions with the methyl groups, possess an exceptionally intense electrophilic action. They more strongly increase the mobility of the hydrogen of the methyl groups linked to them than do the aromatic residues.

4. It was established that, in contrast to the action of electrophilic substituents which, when in conjugation with the methyl group increase the lability of the latter's hydrogens, nucleophilic substituents lower the activity of the methyl group in its reactions with carbonyl, nitroso and diazo compounds.

5. New experimental results are presented which confirm our previous observation that the transition of a hetero atom into the onium state enhances its electrophilic properties. This transition is accompanied by increased mobility of the hydrogens of the methyl groups which are conjugated with the heteroatom.

6. The products of coupling with some diazo compounds of substances containing active methyl groups are described: α-methylpyridine, 2,6-dimethyl-pyridine-3,5-dicarboxylic acid; α-methylimidazole; 2,4,6-trinitrotoluene; 9-methylacridine; and 2-acetylamino-9-methylacridine.

7. The absorption curves are plotted of substances obtained by coupling with p-nitrodiazobenzene and diazobenzene of alkyl halide compounds of 2-methylbenzothiazole and 9-methylacridine, also nonalkylated 9-methylacridine and its 2-acetylamino derivative.

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THE SULFONATION REACTION

XXXII. ISOMERIZATION OF NAPHTHALENE DISULFONIC ACIDS

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Sulfonation of naphthalene gives 6 isomeric disulfonic acids. At a certain temperature and in water contraining sulfuric acid, some isomers may be transformed into others. The process may proceed in the direction of formation of certain isomers to the end or to the setting-up of equilibrium states between them [1].

The phenomenon of reciprocal transition of naphthalene disulfonic acids was observed by Ebert and Merz [2], who noted the transformation of the 2,7-disulfonic acid into the 2,6-isomer at 160°. According to Fierz-David and Hasler [3], up to 27 % of the 2,6-disulfonic acid is obtained at 160°. Isomerization of the 1,5-acid starts below 100°, and it completely disappears from the sulfonic acid mixture after 8 hours at 130°. About 20% of 2,6-isomer is formed when the 1,5- or the 1,6-disulfonic acid is heated with 93% sulfuric acid for 8 hours at 160°. Heating of the 2,6-acid in these conditions leads to formation of the 2,7- and 1,6-isomers. Heid [4] heated the 2,7-isomer in 95% sulfuric acid at 160° and found up to 42% 2,6-acid in the mixture, but his analytical method was very inaccurate. Ambler, Lynch and Scanlan [5] heated the 1,5- and 1,6-isomers at 120° and found the 2,7-isomer in the mixture. After 6 hours at 140°, the 1,6-isomer is almost completely isomerized, mainly to 2,7-isomer.

At 160° the 1,5- and 1,6-acids almost completely change into 2,6- and 2,7-acids. Vorozhtsov and Chuksanova [6] found that sulfonation of naphthalene at 160° gives the following isomers in the order of their yields: after 5 minutes 1,6- and 1,7-; after 30 minutes 1,6-, 2,6-, 2,7-, 1,7-; after an hour 1,7-, 1,6-, 2,7-, 2,6-; after 2 hours 2,7-, 1,7-, 2,6-.

On the basis of the above data it is impossible to detect any regularity in the isomerization of the disulfonic acids. Most chemists are of the opinion that the mechanism of rearrangement consists in hydrolysis of the sulfonic acid and in resulfonation of the products of hydrolysis. The sulfonic acids more stable to hydrolysis then preponderate. In a number of cases the possibility of intramolecular rearrangement is not rejected [6, 7].

On the basis of observations of the velocity of hydrolysis of naphthalene disulfonic acids and of the velocity of sulfonation of monosulfonic acids, Lentz [8] considers that 2,6- and 2,7-disulfonic acids are present in identical quantities in the sulfonated mixture. Heating of 2,6- and 2,7-disulfonic acids in sulfuric acid for 24 hours at 170° leads to an equilibrium state between equal parts of the 2,6- and 2,7- acids. Lantz indicates the possiblity of formation of the 1,6-isomer in addition. On isomerization, however, of the 1,6-acid at 100-130°, the 2,6-isomer was observed to accumulate rapidly and the 2,7-isomer slowly, and this prompted the author to assume the presence of a new isomer, apparently the 1,7-acid. Heating of the 1,5-acid at 100° transforms it into the 1,6-isomer which, in turn, leads to 2,6- and 2,7-isomers.

It is necessary to remember that many experiments were performed by Lantz at a temperature and concentration of sulfuric acid such that either the disulfonic acids were sulfonated to trisulfonic acids or hydrolysis took place with formation of monosulfonic acids; the analytical procedure was also very inadequate, as the author admits.

Consequently, the literature does not report any general rule of transformation of isomeric naphthalene disulfonic acids, and we find only occasional and sometimes conflicting data about their isomerization. In these circumstances, we were prompted to undertake a systematic investigation of the isomerization of naphthalene disulfonic acids.

Isomerization of Naphthalene Disulfonic Acids at 100°

1,5-, 1,6- and 1,7- disulfonic acids were subjected to isomerization in 93.5% sulfuric acid at 100°. Results of experiments on the isomerization of the 1,5-acid are set forth in Table 1; these show that at the start the 1,6-isomer is preferentially formed, but later considerable amounts of 1,3- and 1,7-isomers are formed. The increasing quantities of 1,3- and 1,7-isomers are evidently associated with secondary isomerization of the 1,6-acid which is less stable to hydrolysis than any of the other α,β-isomers. None of the sulfonic acid mixtures was found to contain 2,6- and 2,7- isomers. The content of 1,5-disulfonic acid, determined as xylidine, was higher than that determined as benzidine. The presence in the mixture of the 2,6-acid would have led to the reverse result since its xylidine salt is readily soluble [9].

TABLE 1

Isomerization of Naphthalene-1,5-disulfonic Acid in 93.5% Sulfuric Acid at 100-102°.

No. of expt.	Moles sulfuric acid per mole of disulfonic acid	Duration of heating (hrs.)	Comp. of mixture (% of total sulfonic acids)			
			1,5-acid		1,6-acid	1,3- and 1,7-acids
			As xylidine	As benzidine		
295	3.55	10	93.8	92.4	6.9	0
296	3.64	25	81.2	79.8	9.9	9.6
297	3.47	75	51.9	51.5		
298	6.93	10	91.7	91.0	8.7	0
299	7.01	25	64.9	63.6	22.2	13.6
300	6.99	75	14.8	13.4	45.1	40.8

With progressive reduction in the quantity of 1,5-isomer, the process correspondingly proceeds ever more in the direction of formation of the stable 2,6- and 2,7-isomers and of decrease of the amounts of 1,6-isomer and later of 1,3- and 1,7-isomers.

Consequently, the logical sequel to the isomerization of the 1,5-disulfonic acid is isomerization to the analogous 1,6- and 1,7-acids, results of experiments with which are set forth in Table 2.

TABLE 2

Isomerization of Naphthalene-1,6- and -1,7-disulfonic Acids in Presence of 7 Moles 93.5% Sulfuric Acid at 100-102°

No. of expt.	Isomerization of	Duration of heating (hrs.)	Comp. of mixture (in % of sum of disulfonic acids)				Ratio of 2,7- to 2,6-isomer
			2,6-	2,7-	1,6-	1,3- and 1,7	
302	1.6-	25	1.6	13.6	64.4	20.4	8.5
303	1.6-	75	2.5	23.6	48.4	25.5	9.4
316	1.6-	150	5.5	44.4	24.5	25.6	8.4
317	1.6-	300	7.9	58.1	13.6	20.4	7.4
328	1.6-	760	8.7	75.0	3.8	12.5	8.6
329	1.6-	1200	9.4	77.3	2.3	11.0	8.2
304	1.7-	25	1.8	15.1			8.4
306	1.7-	75	2.1	17.3	39.1	41.5	8.2

In the isomerization of the 1,6-acid it was actually found that the fall in amount of starting substance is accompanied by the appearance of 2,6- and 2,7-disulfonic acids which are not hydrolyzed in these conditions. For direct demonstration of the presence of the latter in the mixture, the disulfonic acids were isolated in the form of benzidine salts and transformed into chlorides which were identified by their melting points.

In all experiments the 2,6- and 2,7-isomers are formed in the approximate ratio of 1:8.5, as we had already noted previously in the sulfonation of the β-sulfonic acid. The data of Table 2 show that the amount of 1,3- and 1,7-isomers attains a maximum of about 26% and then falls off, but not as quickly as the amount of 1,6-isomer. With passage of time the sum of the 1,3- and 1,7-isomers ever more greatly exceeds the quantity of 1,6-acid due to the greater resistance to hydrolysis of the former.

The isomerization of the 1,7-isomer proceeds similarly to that of the 1,6-isomer.

Long-period experiments on isomerization of the 1,6-acid led to sulfonic acid mixtures containing a large amount of 2,7-isomer and a small amount of 2,6-isomer (experiment 328 and 329). Since at 100° all the isomers are hydrolyzed with appreciable speed, apart from the 2,6- and 2,7-isomers, isomerization proceeds irreversibly in the direction of formation of 2,6- and 2,7-isomers depending upon the conditions [1]. If the heating is prolonged much beyond the period of experiment 329, we can obtain a mixture consisting solely of 2,6- and 2,7-acids in the ratio of 1:8.5.

Isomerization of Disulfonic Acids at 130 and 140°

We attempted to accelerate the isomerization of the disulfonic acids by raising the temperature while retaining the initial ratio of 2,6- and 2,7-isomers. For this purpose we performed experiments at 130 and 140°.

The results of the experiments (Table 3) show that isomerization of the 1,5-acid proceeds so rapidly that after 10 hours the starting material could not be detected in the mixture with the help of m-xylidine. Isomerization of the formed 2,6- and 2,7-disulfonic acids was not observed at first, but later (when their amount rises) a change is noted in the original 1:8.5 ratio of the 2,6- to the 2,7-isomer in favor of the 2,6-acid which is the most stable isomer. Just as at 100°, mixtures are obtained with a high content of 2,7-isomer and a low content of 2,6-isomer (expt. 344 and 345).

TABLE 3
Isomerization of Naphthalene-1,5-disulfonic Acid in Presence of 3.5 Moles of 90% Sulfuric Acid at 130°

No. of Expt.	Duration of heating (hours)	Composition of mixture (in % of sum of disulfonic acids)				Ratio of 2,7- to 2,6-acids
		2,6-	2,7-	1,6-	1,3- and 1,7-	
343	10	2.5	20.8	50.6	26.1	8.3
344	25	6.8	55.9	18.1	19.2	8.2
345	35	8.8	66.3	11.3	13.6	7.5
349	50	16.5	61.5	11.8	10.2	3.7

At 130°, just as at 100°, the 1,5-acid gives predominantly the most labile of the α,β-isomers — the 1,6-isomer; subsequent enrichment takes place of the 1,3- and 1,7- and the more stable 2,6- and 2,7-isomers.

Isomerization of the disulfonic acids at 140° proceeds more rapidly than at 130°, which is reflected also in the rapid upsetting of the original ratios between the 2,6- and 2,7-isomers. Experiments were performed with three isomers. The results (Table 4) show that when the 1,5-acid is isomerized the total of 2,6-, 2,7- and 1,7- isomers is higher than when starting out from the 1,6-acid in identical conditions. This shows that in the former case the isomerization is more extensive, although it would appear that it should be reversible since the isomerization of the 1,5-acid is associated from the start with transition into α,β-isomers, whereas the 1,6-acid is already a α,β-isomer. This is explained by the ease of hydrolysis of the 1,5-acid to α-sulfonic acid and naphthalene, which rapidly leads to formation in the mass of β-naphthalenesulfonic acid; the latter is further sulfonated to α,β- and β,β-isomers; there is also rapid accumulation of α,β-isomers formed both by sulfonation of α- and of β-sulfonic acid. Consequently, the more labile is the isomer, the more rapidly and the more extensively does its isomerization proceed in the given conditions.

TABLE 4
Isomerization of Naphthalene Disulfonic Acid in Presence of 3 Moles of 87% Sulfuric Acid at 140°.

No. of Expt.	Isomer	Duration of heating (hours)	Composition of mixture (in % of sum of disulfonic acids)				Ratio of 2,7- to 2,6-acids
			2,6-	2,7-	1,6-	1,3- and 1,7-	
338	1,5	5	4.0	29.1	33.4	33.5	7.3
337	1,5	10	5.6	52.4	15.6	26.4	9.3
340	1,5	15	12.9	48.4			3.7
334	1,6	5	2.7	19.4	50.7	27.2	7.2
335	1,6	10	6.0	48.0	22.8	23.2	8.0
336	1,6	25	17.4	59.8	12.3	10.5	3.4
350	1,7	10	2.6	18.5	47.4	31.5	7.1

Isomerization of Disulfonic Acids at 160°

The 1,6-, 2,6- and 2,7-isomers were subjected to isomerization at 160°. The results of the experiments with the 1,6-acid (Table 5) show that isomerization is much more rapid than at 140°.

The original ratios of 2,6- and 2,7-isomers have already changed appreciably after 5 hours. The experiments also show that isomerization with 3 moles sulfuric acid proceeds more rapidly than with two moles. The same regularity was also observed in experiments with the 1,5-acid at 100° (Table 1). The results of the last three experiments of Table 5 show that the amount of 2,7-isomer rises to a maximum and then falls off while the quantity of 2,6-isomer continuously increases. Consequently, two experiments of this series must be regarded as a continuation of the experiments of the first series (with two moles sulfuric acid) in which the maximum for the amount of 2,7-isomer was not reached. In the experiments of Table 5 a state close to equilibrium between the isomers was not attained.

TABLE 5
Isomerization of Naphthalene-1,6-disulfonic Acid in Presence of 77% Sulfuric Acid at 159-160°.

No. of expt.	Moles sulfuric acid per mole sulfonic acid	Duration of heating (hrs.)	Composition of mixture (in % of sum of disulfonic acids)				Ratio of 2,7- and 2,6-isomers
			2,6-	2,7-	1,6-	1,3 and 1,7-	
330	2.02	2	2.2	20.7	44.8	32.3	9.4
331	2.02	5	13.2	37.4	30.1	19.3	2.7
332	2.03	10	19.0	50.7	17.7	12.6	2.7
333	2.03	25	25.4	57.1	8.9	8.1	2.2
325	3.00	5	15.7	49.5			3.1
326	3.09	10	23.8	59.5	8.6	8.1	2.5
327	3.17	25	28.3	55.7			2.0

In Table 6 are set forth the results of experiments with 2,6- and 2,7-disulfonic acids. These show that the process of isomerization of both isomers is considerably slower than the isomerization of the 1,6-isomer, while the 2,6-isomer, in turn, isomerizes more slowly than the 2,7-isomer. Also, in these cases, the labile isomer is rearranged more rapidly and more far-reachingly, as we already established above. No α,β-isomers were found in the mixture of experiment 307; it must be stated, however, that small amounts of them were present. The experiments showed that heating for 300 hours brings about a state close to equilibrium, since the composition of the sulfonic acid mixture is the same when starting either from the 2,6- or the 2,7-acid. A state close to equilibrium was also reached when starting from a mixture which had contained equal amounts of 2,6- and 2,7-isomers. The results of these experiments (Table 7) show that after heating for 300 hours, a mixture is obtained of the same composition as in the experiments of Table 6 (experiments 319, 321 and 322). Consequently, at 160°, the sulfonic acid mixture has the following composition in the equilibrium state (in %): 2,7-disulfonic acid 49; 2,6-disulfonic acid 31; 1,6-disulfonic acid 9; 1,3- and 1,7-disulfonic acids 11.

TABLE 6

Isomerization of Naphthalene-2,6- and -2,7-disulfonic Acids in Presence of 77% Sulfuric Acid at 158-160°

No. of expt.	Isomer	Moles sulfuric acid per mole sulfonic acid	Duration of heating (hrs.)	Composition of mixture as % of sum of disulfonic acids			
				2,6-	2,7-	1,6-	1,3- and 1,7-
307	2,6	2.01	10	92.5	7.5		
308	2,6	2.05	25	87.7	10.4		1.9
314	2,6	2.03	75	67.0	23.6	1.5	7.9
315	2,6	2.04	150	52.8	34.7	5.0	7.5
319	2,6	3.07	300	31.2	49.5	9.4	10.0
322	2,6	2.92	300	31.3	48.7	9.1	10.9
342	2,7	2.26	10	1.9	88.4		10.9
341	2,7	2.22	25	4.2	78.8	4.4	12.6
312	2,7	2.00	75	19.7	63.6	6.7	10.0
318	2,7	2.06	150	28.2	54.3	7.0	10.5
321	2,7	3.10	300	31.7	48.4	8.3	11.6

During the formation of sulfonic acids, the labile isomers always make their appearance in preponderating amounts, but the subsequent processes of their hydrolysis and resulfonation change the original ratios in favor of the more stable isomers. This does not signify, however, that the quantity of the isomers in the equilibrium mixture (when all the isomers may be hydrolyzed) is determined only by the stability of the isomer, for in dynamic equilibrium the composition of a mixture is governed both by the velocity of hydrolysis and the velocity of formation of the given isomer.

TABLE 7

Isomerization of Equal Parts 2,6- and 2,7-Acids in Presence of 3 Moles 77% Sulfuric Acid at 158-160°

No. of expt.	Duration of heating (hrs.)	Composition of mixture (as % of sum of disulfonic acids)			
		2,6-	2,7-	1,6-	1,3 and 1,7
323	150	28.7	52.9	7.5	10.9
324	300	31.2	49.3	6.1	13.4

Thus, the velocity of formation of the 2,7-isomer is 8.5 times that of the velocity of formation of the 2,6-isomer; in the equilibrium mixture, however, the ratio of 2,7- to 2,6-isomer is 1.58 due to the velocity of hydrolysis of the 2,7-isomer being greater than that of the 2,6-isomer.

Similar considerations apply to the ratios of 1,6-, 1,3- and 1,7-isomers. Although the 1,7- and 1,3- are more stable than the 1,6-isomer, the velocity of their formation is considerably lower, as we showed previously; hence the amount of each of them is less than the amount of 1,6-isomer.

All the isomeric disulfonic acids, apart from the 1,5-isomer, can originate from the β-sulfonic acid. At 160° the 1,5-isomer is present in the mixture in such small amounts that it cannot be detected. It is the most labile of all the isomers and hydrolyzes to the α-acid and naphthalene. The latter is rapidly sulfonated to a mixture consisting mainly of the more stable β-isomer and sulfonating far more quickly than the α-isomer. Consequently there is very little α-acid in the mixture to be sulfonated to the 1,5-acid, and moreover, it sulfonates less readily than the β-acid. The unfavorable conditions for formation of the 1,5-acid and its lability are the causes of its nearly complete absence from the sulfonic acid mixture at 160°.

EXPERIMENTAL

Experiments were run in the following manner: Into a test tube containing an accurately weighed amount of disulfonic acid (with a known content of water of crystallization) were weighed definite amounts of sulfuric acid and water. The test tube was sealed and heated with occasional shaking in an Eijkman apparatus. All the mixtures were homogeneous. The concentration of the sulfuric acid in the mixture was so chosen that at the given temperature it did not sulfonate the disulfonic acids to trisulfonic acids and did not lead to accumulation of monosulfonic acids by hydrolysis. In all the experiments, the heating was followed by determination of the total acidity, since its constancy before and after heating demonstrated the absence of trisulfonation and of accumulation of monosulfonic acids. The experiments were performed in presence of 2-3 moles sulfuric acid (only at 100° was 7 moles sulfuric acid required for complete solution of the 1,5-disulfonic acid). The amounts of individual isomers were determined by our previously described methods [10]. Disulfonic acids were prepared by saponification in an aqueous-alcoholic medium of the disulfochlorides which were purified by crystallization until the melting points were those of the pure products.

SUMMARY

The process of isomerization of 1,5-, 1,6-, 1,7-, 2,6- and 2,7-disulfonic acids of naphthalene was studied at 100, 130, 140 and 160°. It was found that at 100°, the isomerization of the 1,5-, 1,6- and 1,7-disulfonic acids can proceed to the end in the direction of formation of 2,6- and 2,7-isomers which are formed in the ratio of 1:8.5.

At 160° a state close to equilibrium is reached with a content of 49% 2,7-acid, 31% 2,6-acid, 9% 1,6-acid and 11% 1,3- and 1,7-acids.

The relative amounts of isomers in the sulfonic acid mixture are governed by their resistance to hydrolysis and by the relative velocity of their formation. The more amenable an isomer to hydrolysis, the greater the speed of its formation.

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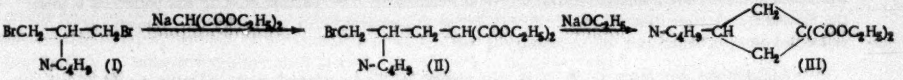
THE SELECTIVE MALONIC SYNTHESIS

III. THE ACTION OF SODIO-MALONIC ESTER ON 1-BROMO-2-BROMOMETHYLHEXANE

V. P. Golmov and N. M. Afanasyev

In previous researches [1, 2] it was shown that in the action of sodio-malonic ester on 1,3-, 1,5-, or 1,6-dihalo derivatives of symmetrical structure, the intermediate product of reaction —haloalkylmalonic ester —may be obtained in a yield of 60 - 70% of the theoretical if a considerable excess of malonic ester and dihalo derivative is used in relation to the amount of sodium ethylate. When, however, sodio-malonic ester acted on 4-bromo-3-bromomethyl-2-methylbutane [3], the yield of γ-bromo-β-isopropyl-propylmalonic ester was only 18% of the theoretical. In addition, a 46% yield was obtained of 1-isopropylcyclobutane-3,3-dicarboxylic ester, which illustrated the great facility with which the intermediate product underwent cyclization. The great ease of cyclization of γ-bromo-β-isopropyl-propylmalonic ester in comparison with γ-bromopropylmalonic ester, however, only applies in the instant of formation, for in the isolated state it is transformed by the action of sodium alcoholate into 1- isopropylcyclobutane-3,3-dicarboxylic ester in the very same yield in which cyclobutane-1,1-dicarboxylic ester is formed from γ-bromopropylmalonic ester (70% of the theoretical).

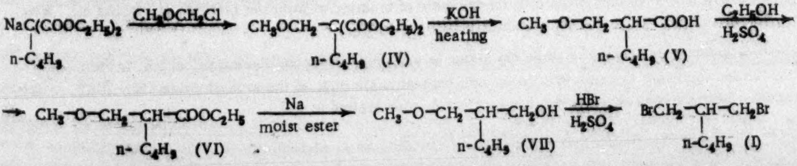
With the aim of establishing whether the yield of haloalkylmalonic ester is also influenced by other radicals located at the second carbon atom of 1,3-dihalo derivatives, we have now carried out the reaction between sodiomalonic ester and 1-bromo-2-bromomethylhexane (I) according to the following equation:



The investigation showed that the n-butyl radical in the molecule of the initial dibromo derivative has also a negative influence on the yield of intermediate product, although to a lesser degree than in the case of the isopropyl group. Thus, using four times as much as the calculated amount of malonic ester and twice as much dihalo derivative, we obtained γ-bromo- β- n-butylpropylmalonic ester (II) in a yield of 40.9% of the theoretical, together with 24.2% of the ester of 1-n-butylcyclobutane-3,3-dicarboxylic acid (III).

The action on isolated γ-bromo-β-n-butylpropylmalonic ester of sodium ethylate gave the ester of 1-n-butylcyclobutyl-3,3-dicarboxylic acid in a yield of 77.6 % of the theoretical, i.e., little different from the yield with which other compounds containing a four-membered ring are formed in the same conditions from the respective γ-haloalkylmalonic esters [2, 4].

The 1-bromo-2-bromomethylhexane (not previously described in the literature) required for the research was synthesized by the method previously developed in the preparation of 4-bromo-3-bromomethyl-2-methylbutane:



$$\underset{n\text{-}C_4H_9}{NaC}(COOC_2H_5)_2 \xrightarrow{CH_3OCH_2Cl} CH_3OCH_2-\underset{n\text{-}C_4H_9\ (IV)}{C}(COOC_2H_5)_2 \xrightarrow[heating]{KOH} CH_3-O-CH_2-\underset{n\text{-}C_4H_9\ (V)}{CH}-COOH \xrightarrow[H_2SO_4]{C_2H_5OH}$$

$$\rightarrow CH_3-O-CH_2-\underset{n\text{-}C_4H_9\ (VI)}{CH}-COOC_2H_5 \xrightarrow[moist\ ester]{Na} CH_3-O-CH_2-\underset{n\text{-}C_4H_9\ (VII)}{CH}-CH_2OH \xrightarrow[H_2SO_4]{HBr} BrCH_2-\underset{n\text{-}C_4H_9\ (I)}{CH}-CH_2Br$$

This method evidently constitutes a general method for preparation of 1,3-dibromo derivatives of similar structure.

Saponification of methoxymethyl-n-butylmalonic ester followed by decarboxylation, as in the previous research [3], gives side by side with β-methoxy-α-n-butyl propionic acid [V] a fairly large amount of α-n-butylacrylic acid. The analogous formation of α-ethylacrylic acid was recently observed by Zakharkin and Preobrazhensky [5] in the decarboxylation of ethoxymethyl-ethylmalonic acid.

EXPERIMENTAL

The starting substances for the investigation were n-butylmalonic ester (prepared by the action of n-butyl bromide on sodio-malonic ester [6]) and distilling at 97-98° at 5 mm) and the monochloromethyl ether with b.p. 55-60° [7].

Methoxymethyl-n-butylmalonic ester (IV). To 34.5 g (1 g-atom) pulverized metallic sodium, under a layer of 900 ml dry ether, was added as quickly as possible 324 g (1.5 mole) n-butylmalonic ester. After the whole of the sodium had dissolved, addition was made to the flask through a dropping funnel, with occasional shaking, of a solution of 150 g monochloromethyl ether in twice the volume of absolute ether. The reaction flask was cooled with water during the addition so that the reaction mixture did not come to the boil. After 24 hours, 800 ml water was added to the flask, the ethereal layer was separated, and the aqueous layer extracted once with ether. The combined ethereal solutions were dried with ignited calcium chloride, the ether was driven off and the residue was fractionated in vacuum. On the average, 18.6 g n-butyl malonic ester was obtained with b.p. 95-102° at 7 mm, and 316 g methoxymethyl-n-butylmalonic ester with b.p. 126-129° at 7 mm. Yield, allowing for the recovered n-butylmalonic ester, is 86.2% of the theoretical.

After a second vacuum distillation the product boiled at 115-116° (4 mm).

d_4^{20} 1.0014; n_D^{20} 1.4312; MR_D 67.13; calculated 67.19.

Found%: C 59.97; H 9.60. $C_{13}H_{24}O_5$. Calculated %: C 60.00; H 9.23.

By this method 1104 g methoxymethyl-n-butylmalonic ester was prepared.

Hydrolysis of methoxymethyl-n-butylmalonic ester. 220 g KOH was dissolved in 480 ml water and to the solution was added 400 ml 95% alcohol. The flask was then heated on an oil bath and to the hot alkali solution was added gradually 340 g methoxymethyl-n-butyl-malonic ester. The reaction mixture was boiled for 5 hours; the alcohol was then distilled off and the cooled residue was extracted once with ether for removal of the unsaponified ester, of which 10 g was recovered.

Addition was then made to the liquid, with cooling, of the calculated amount of sulfuric acid diluted with twice the volume of water. The layer of acids was collected; the aqueous layer was extracted 3 times with ether; the ethereal extracts, combined with the main bulk of product, were dried with ignited calcium chloride and the ether driven off. The residue was decarboxylated by refluxing in an oil bath heated to 160-180°; after CO_2 had ceased to come off, the product was fractionated in vacuum.

Hydrolysis was carried out of 1100 g methoxymethyl-n-butylmalonic ester in this way and 110 g of a fraction with b.p. 94-95° (5 mm) and 440 g with b.p. 121-122° (5 mm) were obtained.

α-n-Butylacrylic acid. The 94-95° (5 mm) fraction was α-n-butylacrylic acid (yield 20.5% of the theoretical [8]).

d_4^{20} 0.9513; n_D^{20} 1.4426; MR_D 35.70; calculated 35.60.

Found %: C 65.48; H 9.58. $C_7H_{12}O_2$. Calculated %: C 65.62; H 9.37.

In ethereal solution the compound adds on one mole of bromine to form the bromide, a viscous oil. When kept in a sealed ampoule it polymerizes to a white, rubbery mass [8].

α-n-Butylacrylamide was prepared by the action of ammonia on the acid chloride, which, in turn, was prepared by the interaction of the acid with phosphorus pentachloride (b.p. of the acid chloride 165-168°). After recrystallization from carbon tetrachloride, α-n-butylacrylamide melted at 69°.

Found %: N 10.84. $C_7H_{13}ON$. Calculated %: N 11.02.

β-Methoxy-α-n-butylpropionic acid (V). The 121-122° (5 mm) fraction, resulting from hydrolysis of methoxymethyl-n-butylmalonic ester, was β-methoxy-α-n-butyl-propionic acid (yield 65% of the theoretical).

d_4^{20} 0.9766; n_D^{20} 1.4330; MR_D 42.56; calculated 42.32.

Found %: C 60.00; H 10.00. $C_8H_{16}O_3$. Calculated %: C 60.00; H 10.00.

Acid chloride of α-n-butylpropionic acid was prepared by the action of phosphorus pentachloride on the acid in the usual manner.

B.p. 175-177°; d_4^{20} 1.0129; n_D^{20} 1.4360; MR_D 46.08; calculated 46.03.

β-Methoxy-α-n-butylpropionamide was prepared by the action of ammonia on a solution of the acid chloride in ether. After recrystallization from ether it had m.p. 72°.

Found %: N 8.50. $C_8H_{17}O_2N$. Calculated %: N 8.80.

Ethyl ester of β-methoxy-α-n-butylpropionic acid (VI) was prepared in the following manner: 226 g β-methoxy-α-n-butylpropionic acid was heated on a water bath for 4 hours with 620 ml absolute alcohol and 62 ml concentrated H_2SO_4.

At the end of the reaction the product was poured into water, the layer of ester was collected; the aqueous layer was extracted with ether; the ether extract was added to the main bulk of product which was washed with water and dried with ignited calcium chloride; the ether was driven off and the residue distilled in vacuum. B.p. 78-79° at 4 mm. Yield 245 g, or 92.3% of the theoretical.

d_4^{20} 0.9186; n_D^{20} 1.4204; MR_D 51.73; calculated 51.57.

Found %: C 64.02; H 10.90. $C_{10}H_{20}O_3$. Calculated %: C 63.83; H 10.64.

β-Methoxy-α-n-butylpropyl alcohol (VII). Into a flask fitted with reflux condenser, dropping funnel, mechanical stirrer and thermometer reaching nearly to the bottom was run 140 ml saturated solution of sodium acetate, 200 ml ether and 63 g (0.33 mole) of the ester of β-methoxy-α-n-butylpropionic acid.

The flask was cooled with a mixture of ice and salt; with slow stirring and at −5 to −2°, 46 g (2 g-atoms) metallic sodium was added and simultaneously (dropwise) 30% acetic acid. The whole addition took about 8 hours. Water was then added until the separated salt had dissolved; the ether layer was separated, and the aqueous layer was extracted three times with ether. The combined ethereal solutions were dried with ignited potassium carbonate; the ether was then driven off, and the residue fractionated in vacuum when a fraction boiling at 91-92° (9 mm) was collected. In the flask remained a considerable amount of thick, dark oil. 418 g ester of β-methoxy-α-n-butylpropionic acid was reduced by the foregoing method to give 232 g β-methoxy-α-n-butylpropyl alcohol. Yield 71.4% of the theoretical.

d_4^{20} 0.8954; n_D^{20} 1.4320; MR_D 42.29; calculated 42.31.

Found %: C 65.79; H 12.10. $C_8H_{18}O_2$. Calculated %: C 65.75; H 12.33.

The p-nitrobenzoate, prepared in the usual manner by the action of p-nitrobenzoyl chloride on the alcohol, had m.p. 194-195° after recrystallization from aqueous alcohol.

1-Bromo-2-bromomethylhexane (I). Into a flask fitted with a reflux condenser were charged 514 g HBr (d = 1.50) and 154 ml sulfuric acid (d = 1.84). To this mixture was added 121 g (0.82 mole) β-methoxy-α-n-butylpropyl alcohol, and the whole was heated at the boil for 10 hours. The liquid darkened considerably during the process. At the conclusion of the heating, the reaction product was distilled off with steam; the lower layer of the distillate was separated, twice shaken with half the volume of concentrated sulfuric acid, washed with sodium carbonate solution, dried with ignited $CaCl_2$ and distilled in vacuum. The sulfuric acid which had been used for washing the crude product was diluted with water and the layer formed (non-reacted β-methoxy-α-n-butylpropyl alcohol) was distilled in vacuum when 15 g came over at 91-98°, (10 mm). 115 g pure 1-bromo-2-bromomethylhexane boiling at 102-103° (11 mm) was obtained; it was a colorless, heavy liquid with a characteristic odor of dibromo compounds. Yield, allowing for recovered starting material, 61.3 % of the theoretical.

d_4^{20} 1.5254; n_D^{20} 1.5000; MR_D 50.40; calculated 50.06

Found %: C 32.60; H 5.49; Br 61.78 (Carius). $C_7H_{14}Br_2$. Calculated %: C 32.56; H 5.42; Br 62.14.

Action of sodio-malonic ester on 1-bromo-2-bromomethylhexane. To a solution of alcoholate prepared from 6.7 g (0.29 g-atom) metallic sodium and 100 ml absolute alcohol was added 186 g (1.16 mole) malonic ester followed by 150 g (0.58 mole) 1-bromo-2-bromomethylhexane. The reaction mixture was left at the normal temperature for 12 hours when a copious white precipitate of sodium bromide came down. The next day the mixture was heated on a bath for 4 hours, the reaction then becoming neutral. While cooling, 0.5 l. water was added, the layer of reaction products was separated; the aqueous layer was extracted with ether; the ethereal extracts were combined with the main bulk of reaction products, which was washed with water, dried with ignited calcium chloride and freed from ether; the residue was fractionated in vacuum through a 20 cm Vigreux column.

Three fractionations gave 226 g of a fraction with b.p. 90-100° at 6 mm (mixture of malonic ester with original dibromo compound), 9 g of a fraction with b.p. 125-130° (1-n-butylcyclobutane-3,3-dicarboxylic ester (III), yield 24.2% of the theoretical), 40 g fraction with b.p. 155-165° (γ-bromo-β-n-butyl-propylmalonic ester (II), yield 40.9% of the theoretical) and 23 g residue. A second distillation of the 125-130° fraction gave b.p. 122-123° (5 mm).

d_4^{20} 1.0024; n_D^{20} 1.4397; MR_D 68.26; calculated 68.36.

Found %: C 65.39; H 9.12. $C_{14}H_{24}O_4$. Calculated %: C 65.62; H 9.37.

After distillation, the 155-165° fraction boiled at 154-155° (4 mm).

d_4^{20} 1.1835; n_D^{20} 1.4603; MR_D 78.03; calculated 77.93.

Found %: C 49.88; H 7.54; Br 23.47 (Carius). $C_{14}H_{25}O_4Br$. Calculated %: C 49.85; H 7.42; Br 23.44.

With the aim of utilizing the recovered starting substances, an experiment was performed in the following manner: To the alcoholate prepared from 6.7 g Na and 100 ml absolute alcohol was added at first 47 g malonic ester (0.29 mole), followed by the 90-100° fraction obtained in the previous experiment. This experiment was repeated three more times; in the first experiment 18 g fraction with b.p. 125-130° at 6 mm and 26 g fraction with b.p. 155-165° were obtained; the second run gave 29 g of 125-130° fraction and 4 g of 155-165° fraction; the third experiment gave 7 g of 125-130° fraction.

In all the four experiments there were used 280 g malonic ester, of which 167 g was recovered unchanged (amount consumed was 113 g or 0.7 mole), 26.8 g (1.12 g-atom) Na and 150 g (0.68 mole) 1-bromo-2-bromomethylhexane. The complete set of experiments gave 65 g (0.25 mole or 43.1% of the theoretical) of the ester of 1-n-butylcyclobutanedicarboxylic acid 70 g (0.21 mole or 36.2% of the theoretical) γ-bromo-β-n-butylpropylmalonic ester, and 38 g distillation residues from which it was impossible to separate any individual substances.

Cyclization of γ-bromo-β-n-butyl-propylmalonic ester. 1.7 g (0.074 g-atom) Na was dissolved in 100 ml absolute alcohol and to the alcoholate solution was added (with cooling) 25 g (0.074 mole) γ-bromo-β-n-butylpropylmalonic ester. After standing at the ordinary temperature for 14 hours, the mixture was heated on a bath at the boil for 2 hours and then poured into 500 ml faintly acidified water; the mass was extracted 3 times with ether; the ethereal extract was washed with water and dried with ignited $CaCl_2$; the ether was driven off and the residue distilled in vacuum. Two distillations in a 20 cm Vigreux column gave 13 g of the ester of 1-n-butylcyclo-butane-3,3-dicarboxylic acid (b.p. 123-125° at 6 mm), and 3 g of the original bromoester (b.p. 155-167° at 6 mm) was recovered. The yield of cyclic product, allowing for the recovered material, is 77.6% of the theoretical.

1-n-Butylcyclobutane-3,3-dicarboxylic acid. 8 g of the ester of 1-n-butylcyclobutane-3,3-dicarboxylic acid was saponified with 20% aqueous alcoholic solution of KOH; the alcohol was distilled off from the solution and the residue was acidified, while cooling, with dilute sulfuric acid solution and extracted several times with ether. The ethereal extract was dried with ignited $CaCl_2$ and the solvent was driven off to leave 6.5 g crystalline acid which, after recrystallization from benzene, melted at 125-126°. Yield 92% of the theoretical.

Found %: C 60.16; H 8.07. $C_{10}H_{16}O_4$. Calculated %: C 60.00; H 8.00.

SUMMARY

1. 1-Bromo-2-bromomethylhexane was synthesized.

2. Treatment of it with sodio-malonic ester (4 moles malonic ester, 2 moles dibromo compound and 1 g-atom sodium) gave: the ester of γ-bromo-β-n-butylpropylmalonic acid in a yield of 40.9% of the theoretical and the ester of 1-n-butylcyclobutane-3,3-dicarboxylic acid in a yield of 24.2% of the theoretical.

3. When sodium alcoholate acts on γ-bromo-β-n-butyl-propylmalonic ester, the latter is transformed into the diethyl ester of 1-n-butylcyclobutane-3,3-dicarboxylic acid in a yield of 77.6% of the theoretical.

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EXPERIMENTAL DETERMINATION OF THE HEIGHT OF THE POTENTIAL BARRIER IN THE HYDROGEN BONDS OF BENZOQUINHYDRONE

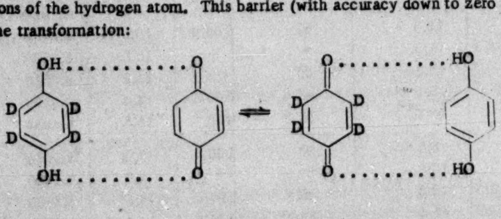
I. P. Gragerov and A. I. Brodsky

The problem of the position and mobility of the hydrogen atom in hydrogen bonds has not hitherto been closely studied. The potential curve of this atom may be represented as the sum of two intersecting curves forming two minima which are separated by a potential barrier. These minima correspond to two equilibrium positions, for example O—H........O and O........H—O and, especially at certain bond lengths, they can merge. The state of the hydrogen atom in hydrogen bonds is governed by the height of this potential barrier. If it is of a certain order of magnitude with zero vibration energy of the O—H (or alternatively of the X—H for the X—H........X bond), then the hydrogen atom very often moves from one position to another and hence is delocalized. At a high potential barrier the localization of this atom is maintained; such transitions as O—H........O⇌O........H—O are, however, possible (a type of tautomeric transformation), depending upon the height of the barrier which governs the energy of activation of this transformation. Finally, with a very high barrier the hydrogen atom is firmly fixed at one of the two atoms (or groups) linked by it.

The theoretical calculation of the height of the potential barrier in question for different hydrogen bonds has been carried out in a series of investigations with extremely conflicting results: from a few kcal/mole [1], for example 2, to 30 and more kcal/mole [2, 3, 4]. The majority of these calculations are based on questionable assumptions which deprive them of any quantitative reliability. This applies above all to the approximation of the potential curve of the X—H........X bond by the Morse function which is here invalid due to the great unharmonicity of the vibrations of the hydrogen bond itself [6]. For this reason the actual parameters selected for the calculation are very untrustworthy. This applies both to the identification of the frequencies, which has hitherto been a controversial point [7], and to the choice of bond lengths. Moreover, the calculated height of the barrier is greatly dependent on the given X—X distances, especially, on the equilibrium position of the hydrogen atom in the bond which, as we know, can still not be reliably measured. A change in the X—X distance by 0.2 A may change the calculated height of the barrier a hundredfold [2]. Furthermore, as was shown by M. I. Batuev [3], the height of the barrier is also highly dependent upon the nature of the end atoms or groups and differs completely from that of the isolated hydrogen bond to which, openly or indirectly, the majority of calculations relate. Finally, we have to remember that when the potential curve is asymmetric, the passage of hydrogen atoms through the barrier is accompanied by marked distortion of this curve due to rearrangement of the electron densities both inside the hydrogen bond and in other parts of the molecule.

We see from the foregoing data that the direct experimental determination of the height of the potential barrier in hydrogen bonds is a matter of considerable interest. Prior to the present investigation, it had never been undertaken. We made use of an isotopic method.

In previous researches one of us and G. P. Miklukhin [5] had shown that in benzoquinhydrone the hydrogen atoms of the hydrogen bonds remain near the hydroquinone nucleus so that the frequently propounded theory of oscillation of the hydrogen atom between two equilibrium positions or the theory of its delocalization is refuted by direct experiment in this case. Since up to now these researches were the sole direct experimental investigation of the problem under consideration, the question still remains open as to whether localization is a specific feature of the hydrogen bonds of benzoquinhydrone or whether it bears a general character. The observed localization of the hydrogen atom in hydrogen bonds points to a considerable height of the potential barrier between two minima corresponding to the two equilibrium positions of the hydrogen atom. This barrier (with accuracy down to zero energy) is equal to the energy of activation of the transformation:



(1)

which may be observed if one of the nuclei of the benzoquinhydrone molecule is labeled with deuterium, as was done in the cited investigations and as is indicated in the equation above.

In the previous investigations the possibility of slow transformation (equation 1) with a high activation energy was suggested. This is confirmed by the data below.

EXPERIMENTAL

The kinetics of reaction (1) may be studied with the help of deuterium because in the course of the reaction the nucleus of heavy hydroquinone is transformed into the nucleus of heavy quinone, while the nucleus of light quinone transformed into the nucleus of light hydroquinone. Consequently fractionation of the reaction product gives quinone containing heavy quinone in an amount which serves as a measure of the course of the reaction.

The benzoquinhydrone from heavy hydroquinone and ordinary quinone [5] were heated in quartz ampoules for a definite time at a given temperature and then separated into quinone and hydroquinone by fractional sublimation in high vacuum at 95°. Fractionation was complete after 45 minues, but after the first 15 minutes about 70% of the substance had been fractionated. The procedure differed from that previously described in that the operation was performed in a quartz vessel with small plugs of cotton wool. This change was dictated by the fact that glass catalyzes the reaction and was responsible for the poor reproducibility of our previous experiments.

In blank experiments with previously unheated quinhydrone, it was found that during the actual sublimation there is slow transfer of deuterium into the quinone, equal in our experimental conditions to 1.8%; the process shows good reproducibility when using identical amounts of material (0.3 g) and when the sublimation conditions are unchanged, as was the case in our investigation (see the first two experiments in Table 1). This correction is reduced in experiments with previously heated quinhydrone in accordance with transformation (1) which continued right up to the fractional sublimation. It is proportional to the degree of transformation before sublimation and it amounted in different experiments to 1.4 to 0.6% D.

Isotopic analysis was performed by the previously described procedure except that a microflotation method was applied which ensured an accuracy of 5% of the determined value and permitted the analysis of 0.04 - 0.05 g water. The initial content of deuterium in the hydroquinone nucleus was 25%.

In Table 1 are set forth the results of kinetic experiments. In addition to the observed percentage passage of deuterium into quinone $\underline{x_1}$, the table gives the magnitude of $\underline{x}$ corrected for the transfer of deuterium during sublimation. The latter served as the basis of further kinetic calculations. As a check, the content of deuterium was determined also in the hydroquinone after fractionation. From the same table we see that both analyses in all cases are in sufficiently good agreement with each other.

TABLE 1

Duration of heating (min.)	Temp. (in °C)	Found % D			Corrected value of $\underline{x}$	$-\ln(1 - x/x_\infty)$
		in quinone (x_1)	in hydroquinone	sum		
0	–	1.8	103	104.8	–	–
0	–	1.8	104	105.8	–	–
109	107.6	6.7	91	97.7	5.3	0.1122
109*		5.6	94.8	100.4	4.1	0.0856
220		10.5	92	102.5	9.4	0.2080
248*		8.2	93.5	101.7	6.9	0.1486
38*	115.1	9.4	93.5	102.9	8.2	0.1792
38		7.3	–	–	6.0	0.1280
60		11.9	92	103.9	10.9	0.2458
82		11.6	–	–	10.6	0.2383
120		15.5	90	105.5	14.8	0.3510
164		15.1	85.4	100.5	14.4	0.3397
164*		17.3	85.8	103.1	16.6	0.4040
20*	119.8	8.5	92	100.5	7.2	0.1548
20		10.0	–	–	8.9	0.1960
58*		15.3	89.1	104.4	14.6	0.3455
58		15.5	89.3	104.8	14.8	0.3510
115		18.0	85.3	103.3	17.4	0.4278

TREATMENT OF RESULTS

Transformation (1) corresponds to a reversible monomolecular reaction obeying the equation:

$$-\ln(1 - x/x_\infty) = Kt, \quad (2)$$

where $K = K_1 + K_2$ — the sum of the velocity constants of the forward and reverse reactions and x_∞ is the limiting equilibrium value of the magnitude $\underline{x}$. Since the replacement of hydrogen by deuterium in the benzene ring cannot substantially influence the energetic and kinetic properties of the investigated system,* then $K_1 = K_2$ and $x_\infty = 0.5$.

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* Heating was performed in nitrogen-filled ampoules.

Note. Duration of sublimation 45 minutes.

The dependence of the magnitude of $-\ln(1 - x/x_\infty)$ on the duration is represented by the experimental points in Fig. 1. We see from this that approximately up to $x = 0.1$, the kinetics of the process satisfactorily accord with equation (2). With more prolonged heating the transfer slows down and the deviation from the equation of the monomolecular action constantly increases. These deviations must be attributed to some secondary reaction whose nature we could not establish. Evidently, connected with this anomaly is another one which was observed in lengthier experiments whose results are set forth in Table 2. We see from this table that not once could values of x exceeding 0.3 be reached.

TABLE 2

Duration of heating (min.)	Temp. (in °C)	Found % D		
		in quinone	in hydroquinone	sum
60**	120°	27.4	74	101.4
1740**	120	26.5	73	99.5
180**	129-130	27.3	69	96.3
480**	129-130	26.8	71	97.8
2450***	120	26.0	75.8	101.8
1800***	115	20.6	77.2	97.8
2450****	120	–	29.8	–
1800****	115	85	17	102

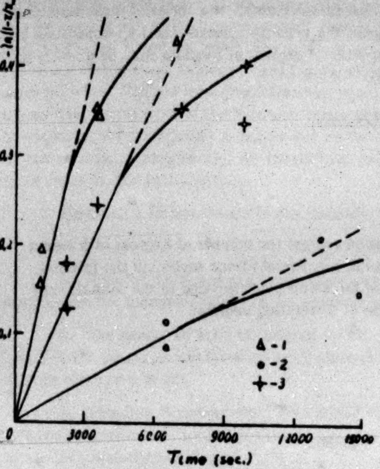

Fig. 1. Dependence of the velocity of transfer of deuterium from hydroquinone to quinone on the temperature. 1 - experiments at 119.8°; 2 - experiments at 107.6°; 3 - experiments at 115.1°

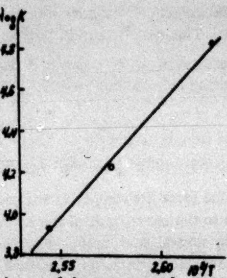

Fig. 2. Dependence of the constant of velocity of transfer of deuterium from hydroquinone to quinone on the temperature.

The further treatment of the experimental data was based on the fields in which these anomalies do not yet take effect, and in accordance with this we adopted for x_∞ the value of 0.5***** indicated above. The analytically interpolated straight lines of Fig. 1, give the following velocity constants K in sec.^{-1}:

Temperature	107.6	115.1	119.8°
K	$0.89 \cdot 10^{-3}$	$3.60 \cdot 10^{-3}$	$7.08 \cdot 10^{-3}$.

The scatter of the experimental points introduces a certain arbitrariness into the choice of slope of the straight lines, but we can readily convince ourselves that the different methods of interpolation, compatible with the experimental data, do not change the value of the activation energy by more than a few percent. We see from Fig. 2 that the values of $\log K = f(1/T)$ fall fairly consistently on a straight line for which we obtained (by the method of least squares):

$$\log K = 24.070 - 11.00 \cdot 10^3\, 1/T. \tag{3}$$

Application of the usual equation with a Boltzmann distribution of energy from two quadratic terms would give, according to (3)

$$K = 1.18 \cdot 10^{24} \cdot e^{-50314/RT}$$

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* This is confirmed by the data of the preceding research [5] and by the data in Table 2.

** Heating in glass. *** Heating in quartz. **** Quinhydrone from ordinary hydroquinone in heavy quinone.

***** Repetition of the calculation with $x_\infty = 0.25$ does not seriously influence the result: the velocity constants are reduced by a factor of 2, while the activation energy increases by less than 2 kcal/mole.

However, the value of 50.3 kcal/mole calculated by this method for the activation energy does not correspond to the actual value due to the application of the simplified energy distribution formula with two quadratic terms for the monomolecular decomposition reaction of such a complex molecule as quinhydrone in which the energy is distributed along many vibrating degrees of freedom. A sufficiently close approximation in such cases is obtained with the equation:

$$K = A\frac{(E/RT)^{m-1}}{(m-1)!}e^{-E/RT} = P \cdot e^{-E/RT} \tag{4}$$

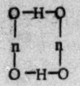
where P is a fore-exponential factor, E is the activation energy and m is the number of vibrating degrees of freedom of the activation energy. It has already been successfully used for the kinetics of a series of monomolecular reactions [8]. For its three parameters we have only two variables: the velocity constant and its temperature coefficient. The relation between the activation energy and the number of degrees of freedom may be directly obtained by comparison of the derivatives for 1/T from (3) and (4).

$$E/RT^2 - \frac{m-1}{T} = 11.00 \cdot 10^3 \cdot 2.3026,$$

from which, for a mean value of T = 387°, we find*

$$E = 50314 + 768.6\,(m-1). \tag{5}$$

For unequivocal determination of the value of the activation energy, the number of degrees of freedom m must be given in addition.** It is plausible to assume that in the benzoquinhydrone molecule the internal vibrations of the nuclei (n) interact weakly with the vibrations of the atoms participiating in the formation of hydrogen bonds. This molecule must then be regarded as a system of 8 vibrating centers:



having m = 8·3 − 6 = 18° of freedom. According to (5) we get E = 63380.

The value found for the activation energy, corresponding to the choice of the number of m, can be regarded as close to the upper limit of the actual value. With a smaller number of degrees of freedom, the latter may be lower by several kcal/mole. The scatter of the experimental points and other sources of error do not introduce an inaccuracy which should exceed the indicated magnitude.

Having substituted in (4) the magnitude log K = −4.354, calculated from (3) for the indicated mean temperature, we find log P = 24.11 + 0.434 (m − 1) or 31.49 for m = 18; hence:

$$K = 3.17 \cdot 10^{13}\frac{(63380/RT)^{17}}{17!}e^{-63380/RT}$$

This equation gives values for K which differ from the experimental ones by not more than 15%.

The high value of the fore-exponential factor, equal to $3 \cdot 10^{31}$ sec^{-1} may depend both on the fact that − in contrast to gaseous reactions − in the crystalline lattice the activation is effected by a transfer of vibratory energy, and on a possible chain mechanism of the propagation of process (1) in this lattice.

The comparatively high value of the activation energy (in round figures 63 kcal/mole) is easily accounted for by the reaction requiring the transfer of an atom of hydrogen in two hydrogen bonds with simultaneous far-reaching rearrangement of the remaining bonds. There is every reason to believe that both transitions take place in a single elementary act (in the kinetic sense). This is in accord with the inability (up to now) to detect the decomposition of benzoquinhydrone to the correspondence semiquinones [9]***.

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* The dependence of log K on 1/T, according to (4), does not appreciably depart from linearity in the considered temperature range.

** For gaseous reactions it is usual to put the magnitude of A as that pressure below which a monomolecular reaction degenerates into a second order reaction [8]. This gives, in principle, the supplementary condition determining the value of m. Such a procedure is evidently here not applicable and its reliability is generally doubtful.

*** Decomposition to semiquinones should also have been manifested in the cited previous investigations and should have caused a more or less far-reaching delocalization of the hydrogen atoms.

Consequently, the height of the potential barrier of the hydrogen bond in benzoquinhydrone is equal to half of the activation energy, i.e. about 32 kcal/mole from the zero level of the valence vibration of OH or about 37 kcal/mole from the bottom of the potential trough of this bond.

For the reasons indicated above, a comparison of the values that we found with the theoretically calculated values do not present great interest, especially since the latter relate to other hydrogen atoms. Attention may be drawn, however, to two recent researchers, M.I. Batuev [3] calculated that the potential barrier of the OHO bond changes from 33.4 kcal/mole for water and 24 kcal/mole for propionic and higher saturated acids to 4.8 kcal/mole for crystalline β-oxalic acid. This author notes that his results agree with the localization of hydrogen bonds in benzoquinhydrone found in a previous investigation [5]. M. A. Kovner and V. A. Chuenkov [4] replaced for Morse function by another one which gave a rounded peak of the potential barrier, lowering its value by 8 kcal/mole. For formic, acetic and isovaleric acids they obtained 22-26 kcal/mole for one interpretation of the spectral frequencies and considerably lower values of 14-16 kcal/mole for other interpretations. They regard the last values as the more probable. We see from these data how strongly the calculated results are influenced by the identification of the spectral frequencies of the hydrogen bonds; this identification still remains uncertain. For the case considered in this study, the uncertainty is aggravated by the lack of X-ray and spectrographic data for benzoquinhydrone and its components. Consequently, we refrain from theoretical calculations aiming at a comparison with the experimental value found in this investigation.

We thank a fellow-worker in our laboratory, G. P. Miklukhin, and Prof. V. A. Roiter for valuable advice.

SUMMARY

1. With the help of deuterium a study was made of the passage of hydrogen atoms from hydroquinone nucleus into the quinone nucleus in the hydrogen bonds of benzoquinhydrone.

2. The energy of activation found for this process was about 63 kcal/mole, which corresponds to a height of the potential barrier of 32 kcal/mole in these bonds, reckoned from the level of zero energy of the valence vibrations of OH.

3. This first experimentally determined value of the potential barrier of the hydrogen bond was compared with the theoretically calculated values which only give a qualitative result due to the uncertainty of the parameters on which they are based.

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STRUCTURE AND PROPERTIES OF CELLULOSE ESTERS. 49.

INVESTIGATION OF THE CONDITIONS OF PREPARATION AND OF THE PROPERTIES OF STABLE DERIVATIVES OF CELLULOSE XANTHIC ACID

L. Aleksandru and Z. Rogovin

The sodium salt of cellulose xanthic acid (cellulose xanthate), the most important intermediate product of the viscose fiber industry, is known to be extremely unstable toward various influences. Cellulose xanthate is rapidly decomposed by the action of inorganic and organic acids, of caustic alkali and even of water. Gradual decomposition of this cellulose ester also takes place in contact with carbon dioxide from the air. The low stability of cellulose xanthate has prompted the investigation of a series of problems associated with the chemical structure of this compound. The preparation of derivatives of cellulose xanthic acid with adequate stability toward the action of saponifying agents and elevated temperature would provide the possibility of embarking on a systematic examination of the chemical structure of cellulose xanthate and, in particular, of the nature of the distribution of the ester groups in not highly esterified cellulose xanthate in dependence on the esterification conditions.

Cellulose xanthate is the sodium salt of an acid ester of the thiolthioncarbonic acid and cellulose. We know that neutral esters are more stable as a rule to the action of saponifying agents than are acid esters. This fact was established also for some neutral esters of thiolthioncarbonic acid with low-molecular alcohols [1]. We therefore suggested that esters of cellulose xanthic acid (1. neutral esters of thiolthioncarbonic acid) and other derivatives of this acid will possess enhanced stability to the action of acids and alkalies. The literature contains only contradictory statements about the preparation of the esters and some other derivatives of cellulose xanthic acid [2, 3]. Several patents have also been published in this field [4]. No references to systematic investigations of the stability of these compounds toward saponifying agents appear in the literature. In this paper we present the results of our own investigations of this subject.

EXPERIMENTAL

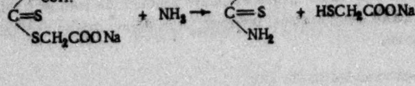
I. Preparation of derivatives of cellulose xanthic acid.

The materials that we selected for study of the stability of derivatives of cellulose xanthic acid toward acids, alkalies and heat were: cellulose xanthoacetic acid, cellulose xanthamide and cellulose methylxanthate.

1) Cellulose xanthoacetic acid was prepared by the action of sodium monochloroacetate on cellulose xanthate present in viscose solution neutralized with 3% acetic acid by the known procedure. When the aqueous solution of the sodium cellulose xanthoacetate is treated with 5% sulfuric acid, a white precipitate of cellulose xanthoacetic acid comes down.

The reaction was performed for 3 hours at 20°; the amount of monochloroacetic acid was 300% of the theoretical. In these conditions, starting from cellulose xanthate with $\gamma = 50$, we obtained a preparation of cellulose xanthoacetic acid with $k\gamma = 25$, which suggests that partial decomposition of the cellulose xanthate occurs in our chosen reaction conditions.

2) Cellulose xanthamide was prepared by reaction of sodium cellulose xanthoacetate in solution with 9 N ammonia solution for 24 hours at 20°. The reaction proceeds according to the following scheme:



$$\mathrm{S{=}C(O\,cell.)(SCH_2COONa)} + \mathrm{NH_3} \rightarrow \mathrm{S{=}C(O\,cell.)(NH_2)} + \mathrm{HSCH_2COONa}.$$

A product was obtained with $\gamma = 25$.

3) The methyl ester of cellulose xanthic acid was prepared by two methods.

a) By conducting the methylation of cellulose xanthate in a heterogeneous medium. The starting material was pure cellulose xanthate. Dimethylsulfate was used as the methylating agent and anhydrous pyridine as the diluent. Following some preliminary experiments, it was established that the optimum conditions for preparation of the product were: duration 6 hours, temperature 20°, amount of dimethylsulfate 500% of the theoretical. In these conditions a product with $\gamma = 25$ was obtained.

b) By conducting the methylation of cellulose xanthate in a homogeneous medium; the reaction follows the same scheme.

When the reaction is performed in a weakly alkaline medium at 20° with 200% of the theoretical amount of dimethylsulfate, cellulose methylxanthate is obtained after only 5 minutes and there is no partial decomposition of the cellulose xanthate. Thus, for example, starting from cellulose xanthate with $\gamma = 50$, in these reactions a cellulose methylxanthate is obtained with the same degree of esterification. We also prepared cellulose methylxanthate with $\gamma = 75$ and $\gamma = 150$, starting from cellulose xanthate with the corresponding degree of esterification.

All our preparations of derivatives of cellulose xanthic acid, with $\gamma = 25$ to 50, are insoluble in caustic alkali and in other accessible solvents.

II. Investigation of the stability of derivatives of cellulose xanthic acid to the action of various reagents

1) Comparative investigation of the stability of derivatives of cellulose xanthic acid, cellulose xanthate, and cellulose acetate toward saponifying agents. It is a matter of great interest to compare the stability of the derivatives of cellulose xanthic acid that we prepared toward the action of saponifying agents (1 N solution of sulfuric acid and potassium hydroxide) as well as toward water at higher temperatures on the one hand with the stability of other industrially important cellulose esters on the other hand (in particular cellulose acetate, also cellulose xanthate). Our results are set forth in Table 1 and Figs. 1, 2 and 3.

TABLE 1*

Reagent used	Duration of treatment (in min.)	Amount of saponified ester groups (in % of original)				
		Cellulose xanthate	Cellulose xanthoacetate	Cellulose xanthamide	Cellulose methyl xanthate	Cellulose acetate
1N H_2SO_4	15	After treatment for 1-2 min. 100	7.35	3.3	14	6.9
1N H_2SO_4	30		20.6	12.6	32	15
1N H_2SO_4	60		74.2	51.5	80.2	39
1N NaOH	15	After treatment for 1-2 min. 100	16.8	15.9	18.1	12.8
1N NaOH	30		74.8	38	80	27
1N NaOH	60		86	78	100	63
Water	60	93.8	3.3	1.1	7	0
Water	120	–	5.4	5.5	12	–
Water	240	–	–	15.4	23.6	–
Water	360	–	–	–	35.2	–

From the data of Table 1 and Figures 1, 2 and 3, we can draw the following conclusions: a) neutral esters of thiolthioncarbonic acid are many times more stable toward saponifying agents than acidic esters of the same acid; b) the stability of derivatives of cellulose xanthic acid changes in dependence on the character of the radicals entering into the composition of the molecule in their preparation. It must be noted, however, that even the least stable derivatives of cellulose xanthic acid are many times more stable than cellulose xanthate: c) all the derivatives of cellulose xanthic acid that we prepared are less stable toward saponifying agents than cellulose acetates, although the difference in stability of these cellulose esters is not very large.

2) Stability of derivatives of cellulose xanthic acid to heat (100°). The data obtained are set forth in Table 2.

It is seen from the data of Table 2, that cellulose xanthamide is more stable to high temperature than cellulose methylxanthate. The degree of esterification, however, of cellulose methylxanthate, also changes insignificantly when it is heated at 100° for 3 hours.

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* All the investigations were carried out at 100°.

TABLE 2

Duration of heat-ing (hrs.)	Amount of saponified ester groups (in % of original)	
	cellulose xanthamide	cellulose methylxanthate
3	0	5.1
6	0	13.65
12	2.2	32.1
18	27.5	59

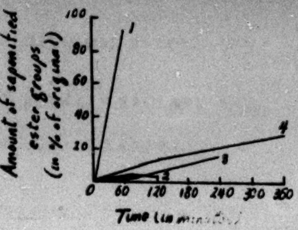

Fig. 3. Stability toward action of water at 100°. 1) Cellulose xanthate; 2) cellulose xanthoacetic acid; 3) cellulose xanthamide; 4) cellulose methylxanthate.

3) Stability of derivatives of cellulose xanthic acid on prolonged storage and on exposure to bright light. Specimens of cellulose methylxanthate were kept at room temperature (20-30°) in a closed box without access to air. After storage for 90 days, the chemical composition of the cellulose methylxanthate had scarcely changed. The number of methyl groups had dropped from 3.52 to 3.19%. After the specimens of cellulose methylxanthate had been kept for 60 days with alternating exposure to moisture and bright light, partial saponification of the ester groups took place. In these conditions 19.83% of the total ester groups are saponified. This change is apparently due to oxidation processes since esters of xanthic acids, as well as xanthate, contain the $>C=S$ group which is clearly unstable towards oxidizing action. We know, however, that ultraviolet rays bring about gradual saponification also of other cellulose esters, such as cellulose acetate and, especially, nitrocellulose.

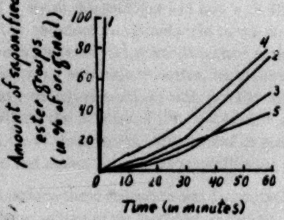

Fig. 1. Stability toward the action of 1 N sulfuric acid at 100°. 1) Cellulose xanthate; 2) cellulose xanthoacetic acid; 4) cellulose methylxanthate; 5) cellulose acetate.

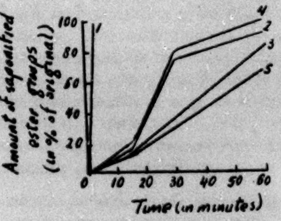

Fig. 2. Stability toward the action of 1 N NaOH at 100°. 1) Cellulose xanthate; 2) cellulose xanthoacetic acid; 3) cellulose xanthamide; 4) cellulose methylxanthate

SUMMARY

1. With the objective of establishing the possibility of preparing stable derivatives of cellulose xanthic acid, the following compounds were prepared and examined: a) cellulose xanthoacetic acid; b) cellulose xanthamide; c) cellulose methylxanthate.

2. It was shown that alkyl esters of cellulose xanthic acid (i.e., neutral esters of thiolthioncarbonic acid), as well as other derivatives of cellulose xanthic acid such as cellulose xanthoacetic acid and cellulose xanthamide, are considerably more resistant to the action of saponifying agents, to thermal action and to prolonged storage than acid salts of thiolthioncarbonic acid, and in particular than the sodium salt of cellulose xanthic acid.

The stability of esters of cellulose xanthic acid toward the foregoing treatments approximates that of other cellulose esters, for example cellulose acetate.

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STRUCTURE AND PROPERTIES OF CELLULOSE ESTERS. 50.

DISTRIBUTION OF THIOCARBONIC GROUPS BETWEEN PRIMARY AND SECONDARY ALCOHOLIC GROUPS IN CELLULOSE XANTHATE

L. Aleksandru and Z. Rogovin

Elucidation of the problem of the nature of the arrangement of thiocarbonic groups in the elementary chain of the cellulose xanthate macromolecule has great importance in the study of the chemical homogeneity of cellulose xanthate and of the effect of the esterification conditions on the properties of the resultant viscose solutions. Up to recently, the experimental study of this problem had met with difficulties due to the poor stability of the thiocarbonic group introduced into the cellulose macromolecule in the process of xanthation. After stable derivatives of cellulose xanthic acid had been prepared, the possibility arose of determining the position of the ester groups in not-fully-esterified cellulose xanthates. With this objective, we prepared a cellulose xanthate with $\gamma = 50$ by xanthation in normal conditions and also a cellulose xanthate with $\gamma = 100$ by supplementary esterification of cellulose xanthate in solution. In cellulose xanthate the position of the thiocarbonic groups is fixed by their methylation [1] which considerably increases the stability of these esters. We decided to prepare cellulose methylxanthate because in the preparation of this product, as we had shown [1], partial saponification of the thiocarbonic groups does not take place.

In cellulose methylxanthate the distribution was determined of the methylthiocarbonic groups between the primary and secondary alcoholic groups of the cellulose molecule. This investigation was performed with application of the method of tritylation of cellulose methylxanthate. As we know [2, 3], triphenylchloromethane selectively and completely esterifies the primary alcohol groups of cellulose in the 6-position with formation of the monotrityl ester of cellulose.

Preliminary experiments showed that the tritylation reaction (when performed without access of air) does not change the chemical composition of cellulose methylxanthate.

An attempt to utilize the method of treatment with iodic acid (which selectively and completely oxidizes the secondary alcoholic groups of cellulose in the 2- and 3-positions to aldehyde groups) for clarification of our problem did not meet with success. Treatment with iodic acid led to partial saponification of the methylthiocarbonic groups.

EXPERIMENTAL

1. Preparation of the mixed ester, cellulose tritylmethylxanthate. Cellulose methylxanthate was prepared by the previously described method [1]. Treatment of cellulose methylxanthate with triphenylchloromethane in presence of pyridine (which binds the evolved HCl) at 110° for 12 hours in absence of air gives the mixed ester, cellulose tritylmethylxanthate. We were the first to prepare this ester.

In our selected reaction conditions, the process of tritylation proceeds to the end. Increasing the esterification period to 20 hours did not change the content of trityl groups in the prepared mixed ester.

The mixed ester, cellulose tritylmethylxanthate, was obtained in the form of a dark-brown powder, difficultly soluble in pyridine. It is insoluble in other solvents. It decomposes at 127-129° with evolution of gases.

II. Determination of the ratio in the cellulose macromolecule of the primary and secondary alcohol groups esterified during the process of xanthation. During the investigation determinations were made of: a) the content of sulfur in cellulose xanthate used for preparation of cellulose methylxanthate; b) the content of sulfur and methyl groups in cellulose methylxanthate; c) the content of sulfur and trityl groups in the mixed ester, cellulose tritylmethylxanthate. Sulfur was determined by oxidation to sulfuric acid with a mixture of potassium permanganate and sodium carbonate [4]. Methyl groups were determined by the micro method of Vieböck and Brecher [5]. The cellulose xanthate that we used contained 14.9% sulfur, i.e., the product had $\gamma = 50$. The cellulose methylxanthate contained 15.1% sulfur and 3.72% methyl groups, i.e., $\gamma = 50$.

Consequently, the thiocarbonic groups were not saponified in the preparation of cellulose methylxanthate. The fact that the content of sulfur and methyl groups corresponds to one and the same γ, shows that all the methyl groups were linked through sulfur.

In the mixed ester, cellulose tritylmethylxanthate, the trityl groups were determined by saponification of the prepared mixed ester with sulfuric acid [6]. From the amount of sulfur present in this product, a determination was made of the total amount of methylthiocarbonic groups linked to the alcohol groups of cellulose in the mixed ester.

Since triphenylchloromethane selectively and completely esterifies the primary alcoholic groups of cellulose in the 6-position, the number of trityl groups is a measure of the number of substituted primary alcohol groups in the cellulose methylxanthate, and we can accordingly calculate from them the number of methylthiocarbonic groups linked in cellulose methylxanthate with the primary alcohol groups in the 6-position. From the difference between the total number of methylthiocarbonic groups in the investigated preparation and the number of these groups linked with the primary alcoholic group, we can determine the number of methylthiocarbonic groups linked with secondary alcoholic groups of the cellulose macromolecule in the 2- and 3-positions. The results are set forth in the table.

Starting product	Sulfur content				Content of trityl groups		No. of thiocarbonic groups (per 100 glucose residues)	
	in cellulose methylxanthate		in cellulose tritylmethylxanthate					
	in %	γ (for methylthiocarbonic groups)	in %	γ (for methylthiocarbonic groups)	in %	γ (for trityl groups)	at primary alcohol groups	at secondary alcohol groups
Cellulose	–	–	–	–	62.3	101	–	–
Cellulose xanthate with $\gamma = 50$	15.1	50	7.43	50	51.08	90	10	40
Cellulose xanthate with $\gamma = 100$	25.67	100	14.9	100	42.53	80	20	80

We see from the data in the table that the degree of esterification of cellulose methylxanthate does not change during the process of tritylation. The data show that during the xanthation reaction carried out as in normal technological conditions, as well as during supplementary xanthation in solution, 80% of the total number of thiocarbonic groups are linked with secondary alcohol groups in the 2- or 3-positions and only 20% of the thiocarbonic groups are linked with primary alcohol groups in the 6-positions.

In our opinion, this conclusion presents considerable interest because it clearly shows that in a number of cases the secondary alcohol groups of the cellulose macromolecule may be more reactive than primary alcohol groups during the esterification process.

It may be suggested that in the course of cellulose esterification reactions proceeding in an alkaline medium, the alcohol groups at the carbon atom in the 2-position (i.e., in the α-position to the carbon participating in the acetal bond and therefore possessing more acidic qualities) will be more reactive than the primary alcohol groups. This suggestion is confirmed by the results that we obtained when investigating the chemical structure of not-highly-esterified cellulose xanthates, as well as in some degree by the results recently obtained in the investigation of the structure of alkali cellulose [7].

SUMMARY

1. The mixed ester, cellulose tritylmethylxanthate, was prepared for the first time for the purpose of investigation of the distribution of thiocarbonic groups between the primary and secondary alcohol groups in the cellulose xanthate macromolecule.

2. The ratio between primary and secondary alcohol groups substituted during the xanthation of the cellulose macromolecule was determined.

3. It was shown that in the process of xanthation of cellulose both the primary and the secondary alcohol groups may react, but the secondary alcohol groups are the more reactive.

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SYNTHESIS OF SOME CHLOROPHENOXY DERIVATIVES

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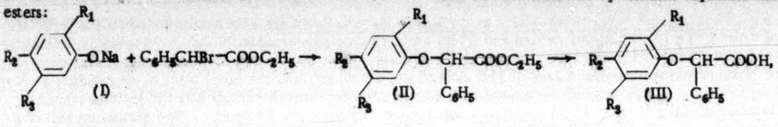
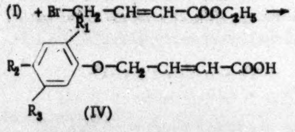
A very large number of diverse substituted aryloxyalkane carboxylic acids have recently been synthesized and tested as plant growth promoters and herbicides. Much work in this field has been carried out in the Soviet Union by the late Academician S. S. Nametkin, N. N. Melnikov and their co-workers [1]. We may claim that the relation between physiological activity and chemical structure in this series has been very closely studied. However, some aspects of the subject have not been adequately clarified. One of these is the influence of the presence of a phenyl group in the α-position of ring-substituted phenoxyacetic acids on their activity. Since there is evidence that the action of heteroauxin as a rooting stimulant is enhanced under the action of phenylacetic acid [2], it was expedient to establish whether the phenyl group intensifies the activity of chlorophenoxyacetic acids. In the literature there is only one reference to this subject, namely that α-(chlorophenyl)-phenoxyacetic acid possesses a low activity [3], but the influence of the unsubstituted phenyl group has not been studied. For this purpose we synthesized α-(4-chlorophenoxy)-, α-(2,4-dichlorophenoxy)- and α-(2,5-dichlorophenoxy)-phenylacetic acids, none of which has previously been described in the literature. These compounds were prepared by interaction of ethyl α-bromophenylacetate with the appropriate phenolates in an alcoholic medium followed by alkaline saponification of the esters:



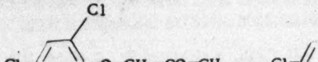
where R_1, R_2 and R_3 = H or Cl.

Specific interest also attaches to the problem of the activity of chlorophenoxycarboxylic acids containing a double bond in the side chain. In this connection it is interesting to note that α-naphthylvinylacetic acid is an active stimulator of root formation [4]. The chlorophenoxycrotonic acids required for settlement of this question were synthesized by condensation of γ-bromocrotonic acid esters with the appropriate phenolates followed by saponification of the resultant esters of γ-chlorophenoxycrotonic acids:

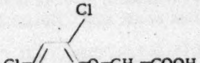


In this way we prepared γ-(4-chlorophenoxy)-, γ-(2,4-dichlorophenoxy)- and γ-(2,5-dichlorphenoxy)-crotonic acids.

Finally, taking into account the fact that in a number of cases the substitution of the hydroxyl group in the molecule of the physiologically active carboxylic acid by a methyl group, i.e., the transformation of the acid into the corresponding methylketone, leads to formation of an antagonist, we effected the synthesis of 2,4-dichlorophenoxyacetone (V), a possible antagonist of 2,4-dichlorophenoxyacetic acid (VI)



(V)



(VI)

2,4-Dichlorophenoxyacetone was prepared by the reaction of potassium 2,4-dichlorophenate with bromoacetone.

Finally, it is our pleasant duty to extend our profound thanks to Academician V. M. Rodionov for his constant interest in this research.

EXPERIMENTAL

Ethyl α-bromophenylacetate was prepared by the procedure of V. M. Rodionov, N. N. Suvorov and K. S. Mikhailov [5]. 2,4-Dichlorophenol was prepared by direct chlorination of 2,5-dichloroaniline followed by replacement of diazo group by hydroxyl [7]. The ethyl and methyl esters of γ-bromocrotonic acid were prepared by bromination of the respective crotonic esters with N-bromosuccinimide [8].

Ethyl ester of α-(4-chlorophenoxy)-phenylacetic acid (II, $R_1=R_3=H$, $R_2=Cl$). To a solution of 6.17 g (0.11 mole) KOH in 60 ml absolute alcohol was added at first 12.9 g (0.1 mole) p-chlorophenol, and then 24.3 g (0.1 mole) ethyl α-bromophenylacetate. After standing for an hour at room temperature the reaction mixture was refluxed for 6 hours. The alcohol was then driven off, water was added to the residue until complete solution occurred of the KBr which had separated during the reaction, the oily layer was separated and the aqueous layer was twice extracted with ether. The ethereal extracts were combined with the main bulk of product and dried over anhydrous sodium sulfate. The ether was driven off and the residue was distilled in vacuum to give a fraction with b.p. 174-178° at 3 mm. Yield 19.1 g (66% of the theoretical). After a second distillation the substance crystallized on standing. M.p. 36-37°.

Found %: C 65.91, 65.98; H 5.36, 5.27. $C_{16}H_{15}O_3Cl$. Calculated %: C 66.10; H 5.16.

α-(4-Chlorophenoxy)-phenylacetic acid (III, $R_1=R_3=H$, $R_2=Cl$). 5 g (0.017 mole) ethyl ester of α-(4 chlorophenoxy)-phenylacetic acid is saponified by boiling with an alcoholic solution of 1.44 g (0.025 mole) KOH for 7 hours. The alcohol is driven off; the residue is dissolved in water and filtered; impurities are extracted with ether. The aqueous layer is acidified with hydrochloric acid (1:2). The precipitate is drained at the pump, washed with water and dried. Yield 4.2 g (61% of the theoretical). M.p. 160.5-161.5° (from toluene).

Found %: C 63.82, 63.79; H 4.37, 4.35. $C_{14}H_{11}O_3Cl$. Calculated %: C 64.00.

α-(2,4-Dichlorophenoxy)-phenylacetic acid (III, $R_1 = R_3 = H$, $R_2 = Cl$). To a solution of sodium ethylate prepared from 0.95 g (0.04 g atom) sodium and 30 ml absolute alcohol was added 6.7 g (0.04 mole) 2,4-dichlorophenol and then 10 g (0.04 mole) ethyl α-bromophenylacetate. After standing for 30 minutes at room temperature, the mixture was refluxed for 6 hours. The alcohol was driven off, and the ethyl ester of α-(2,4-dichlorophenyloxy)-phenylacetic acid was carefully extracted with ether. The ether was driven off and the residue saponified with a solution of 3.5 g KOH in 10 ml absolute alcohol (room temperature, 24 hours). The potassium salt of α-(2,4-dichlorophenoxy)-phenylacetic acid was dissolved in water and the solution made acid (to Congo) with hydrochloric acid. Yield 7.1 g (58.2% of the theoretical). M.P. 130.5-131.5°, rising to 134-134.5° after recrystallization from toluene.

Found %: C 56.93, 56.85; H 3.27, 3.43. $C_{14}H_{10}O_3Cl_2$. Calculated %: C 56.56; H 3.36.

Ethyl ester of α-(2,5-dichlorophenoxy)-phenylacetic acid (II, $R_1=R_3=Cl$, $R_2=H$). To a solution of sodium ethylate, prepared from 1.7 g (0.07 g-atom) sodium in 50 ml absolute alcohol, is added 12.18 g (0.07 mole) 2,5 dichlorophenol followed by 17 g (0.07 mole) ethyl α-bromophenylacetate. The reaction mixture is kept for an hour at room temperature and then boiled for 6 hours. The alcohol is driven off. The residue is extracted with absolute ether and the ether driven off, leaving a solid yellow residue. Recrystallization of the latter from methyl alcohol gives 16.62 g (73.2 % of the theoretical) ethyl ester of α-(2,5-dichlorophenoxy)-phenylacetic acid. M.p. 48°.

Found %: C 59.13, 58.99; H 4.44, 4.55. $C_{16}H_{14}O_3Cl_2$. Calculated %: C 59.10; H 4.34.

α-(2,5-Dichlorophenoxy)-phenylacetic acid. (III, $R_1=R_3=Cl$, $R_2=H$). 6 g (0.018 mole) ethyl ester of α-(2,5-dichlorophenoxy)-phenylacetic acid is saponified with a solution of 1.54 g (0.02 mole) KOH in a mixture of 6 ml alcohol and 15 ml water (refluxed for 6 hours). The reaction mixture is poured into 150 ml water and filtered; the filtrate is acidified (to Congo) with hydrochloric acid. The resultant precipitate is drained at the pump and twice crystallized from acetic acid. Yield 3.3 g (58% of the theoretical). M.p. 122-123°.

Found %: C 57.00, 57.15; H 3.53, 3.44. $C_{14}H_{10}O_3Cl_2$. Calculated %: C 56.56; H 3.36.

γ-(4-Chlorophenoxy)-crotonic acid. (IV, $R_1=R_3=H$, $R_2=Cl$). To a solution of sodium ethylate, prepared from 0.91 g (0.0395 g-atom) sodium and 15 ml absolute alcohol, is added a solution of 5.08 g (0.0395 mole) p-chlorophenol in 10 ml absolute alcohol, followed by 7.6 g (0.0395 mole) ethyl γ-bromocrotonate. After standing for 3 hours at room temperature, addition is made to the reaction mixture of a solution of 2.73 g (0.048 mole) KOH in 20 ml absolute alcohol. After 24 hours the mixture is poured into water, filtered and acidified with hydrochloric acid (to Congo). The residue is drained, washed and dried. Recrystallization from ligroin gives 3.85 g (46.4 % of the theoretical) of a substance with m.p. 96-97°.

Found %: C 56.66, 56.80; H 4.21, 4.38. $C_{10}H_9O_3Cl$. Calculated %: C 56.76; H 4.29.

γ-(2,4-Dichlorophenoxy)-crotonic acid. (IV, $R_1=R_2=Cl$, $R_3=H$). To a solution of 2.8 g (0.05 mole) KOH in 30 ml absolute alcohol is added 8.1 g (0.05 mole) 2,4-dichlorophenol, followed by 8.75 g (0.05 mole) methyl γ-bromocrotonate. After standing at room temperature for 24 hours, the precipitated KBr is filtered off and to the filtrate is added a solution of 2.76 g (0.05 mole) KOH in 30 ml absolute alcohol; the mass is again stood at room temperature for 24 hours. The reaction mixture is poured into water and the impurities extracted with ether. The solution is acidified (to Congo) with hydrochloric acid (1:1), the precipitated acid is drained, dried and twice recrystallized from heptane. Yield 3 g γ-(2,4-dichlorophenoxy)-crotonic acid (24.5% of the theoretical) with m.p. 113-114°.

Found %: C 49.47, 49.26; H 3.47, 3.38. $C_{10}H_8O_3Cl_2$. Calculated %: C 48.58; H 3.25.

γ-(2,5-Dichlorophenoxy)-crotonic acid. (IV, $R_1=R_3=Cl$, $R_2=H$). To a solution of sodium ethylate, prepared from 0.67 g (0.029 g-atom) sodium and 15 ml absolute alcohol, is added, first, a solution of 4.8 g (0.029 mole) 2,5-dichlorophenol in 10 ml absolute alcohol, and then 6 g (0.03 mole) ethyl γ-bromocrotonate. After standing for 3 hours at room temperature, addition is made of a solution of 1.79 g (0.032 mole) KOH in 15 ml absolute alcohol, and the mixture is stood at room temperature for 24 hours. The mixture is then poured into 500 ml water, filtered, and acidified (to Congo). The acid, first precipitated in the form of an oil, rapidly crystallizes. It is drained, washed, dried and twice crystallized from heptane. Yield 4.34 g (63%). M.p. 99.5-100.5°.

Found %: C 49.21, 49.09; H 3.41, 3.26. $C_{10}H_8O_3Cl_2$. Calculated %: C 48.58, H 3.25.

2,4-Dichlorophenoxyacetone (V). To a solution of 2.8 g (0.05 mole) KOH in 25 ml methyl alcohol is added 8.2 g (0.05 mole) 2,4-dichlorophenol, followed by 4.7 ml (0.054 mole) bromoacetone. Heat is developed and KBr is precipitated. The reaction mixture is allowed to stand for 24 hours at room temperature; the precipitate is drained and washed with ether; the solvent is driven off from the filtrate. The residual oil is distilled in vacuum. Yield 6.75 g (61.5% of the theoretical). B.p. 140° at 4 mm. The distillate rapidly crystallizes. M.p. 53-54°. Crystallization from aqueous alcohol gives fine, colorless needles with m.p. 54-55°.

Found %: C 49.47, 49.65; H 3.80, 3.60. $C_9H_8O_2Cl_2$. Calculated %: C 49.45; H 3.65.

2,4-Dichlorophenoxyacetone semicarbazone, prepared by the usual method, forms colorless, fine crystals with m.p. 180-181°.

Found %: N 15.18, 15.01. $C_{10}H_{11}O_2N_3Cl_2$. Calculated %: N 15.21.

SUMMARY

The following were synthesized: α-(4-chlorophenoxy)-phenylacetic acid; α-(2,4-dichlorophenoxy)-phenylacetic acid; α-(2,5-dichlorophenoxy)-phenylacetic acid; γ-(4-chlorophenoxy)-crotonic acid; γ-(2,4-dichlorophenoxy)-crotonic acid; γ-(2,5-dichlorophenoxy)-crotonic acid; and 2,4-dichlorophenoxyacetone.

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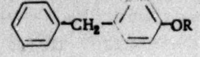
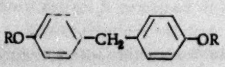
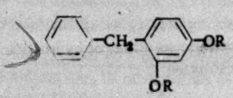
SYNTHESIS OF SUBSTITUTED HYDROXY- AND DIHYDROXYDIPHENYLMETHANES

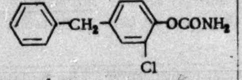
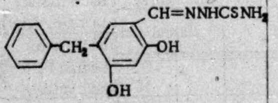
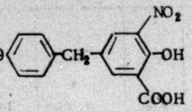
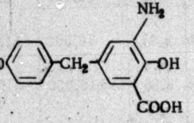
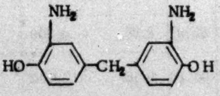
M. V. Rubtsov, E. E. Mikhlina and L. A. Pelenitsina

Diphenylmethane is known to possess bactericidal properties [1]. Taking into consideration the intensification of bactericidal action on introduction of hydroxyl or alkoxy groups, we synthesized a series of ethers of 4-hydroxydiphenylmethane, 4,4'-dihydroxydiphenylmethane and 2,4-dihydroxydiphenylmethane, also derivatives of diphenylmethane containing (in addition to hydroxyl groups) nitro, amino, formyl and carboxy groups. The prepared substances, their physical properties, results of analyses, and *in vitro* activity toward *Trichophiton gypseum* (trichophyton) and *Mycobacterium tuberculosis* (bacillus of human tuberculosis) are set forth in the table.

No.	Formula	Temperature		Empirical formula	Analytical results (in %)				Bacteriostatic activity in vitro, dilution 1:x	
		Of boiling	Of melting		Found		Calculated		bacillus of human tuberculosis x	trichophyton x
					C	H	C	H		
1	2	3	4	5	6	7	8	9	10	11
										
1	R = n-C_3H_7	177-179° (5 mm)	–	$C_{16}H_{18}O$	84.86	7.94	84.95	7.96	32,000	52,000
2	n-C_4H_9	184-186 (8 mm)	–	$C_{17}H_{20}O$	84.88	8.24	85.00	8.33	16,000	512,000
3	iso-C_5H_{11}	188-192 (11 mm)	–	$C_{18}H_{22}O$	85.03	8.31	85.04	8.66	512,000	512,000
4	$CH_2-CH=CH_2$	188-189 (15 mm)	–	$C_{16}H_{16}O$	85.53	6.97	85.76	7.14	512,000	512,000
5	n-C_6H_{13}	213-215 (13 mm)	–	$C_{19}H_{24}O$	85.26	8.98	85.07	8.95	4,000	1,000
6	n-C_8H_{17}	240 (19 mm)	30°	$C_{21}H_{28}O$	85.21	9.32	85.13	9.46	512,000	1,000
										
7	R = n-C_3H_7	220-222 (15 mm)	27	$C_{19}H_{24}O_2$	80.37	8.56	80.28	8.45	16,000	2,000
8	n-C_4H_9	223-224 (5 mm)	33	$C_{21}H_{28}O_2$	80.76	8.78	80.77	8.97	512,000	64,000
9	iso-C_5H_{11}	223-225 (3 mm)	36	$C_{23}H_{32}O_2$	81.25	9.22	81.18	9.41	1,638,000	1,024,000
10	n-C_8H_{17}	245 (5 mm)	45	$C_{29}H_{44}O_2$	82.12	10.30	82.07	10.37	256,000	0
										
11	R = CH_3	178 (7 mm)	–	$C_{15}H_{16}O_2$	78.60	7.08	78.95	7.02	>512,000	64,000

(continued)

Table -- (continued)

1	2	3	4	5	6	7	8	9	10	11
12	R = C_2H_5	174-176 (4 mm)	–	$C_{17}H_{20}O_2$	79.54	8.06	79.67	7.81	1,638,000	1.124,000
13	n-C_3H_7.	201-203 (5 mm)	–	$C_{19}H_{24}O_2$	80.16	8.58	80.28	8.45	>256,000	8,000
14	n-C_4H_9	205-208 (4 mm)	–	$C_{21}H_{28}O_2$	80.37	8.63	80.77	8.97	256,000	16,000
15	iso-C_5H_{11}	221-224 (7 mm)	–	$C_{23}H_{32}O_2$	81.23	9.18	81.18	9.41	>512,000	64,000
16	n-C_8H_{17}	235-240 (5 mm)	–	$C_{29}H_{44}O_2$	82.12	10.14	82.07	10.37	256,000	1,000
17		–	141-142°	$C_{14}H_{12}O_2NCl$	5.38*	13.50***	5.35*	13.57***	–	–
18		–	207-208	$C_{15}H_{15}O_2N_3S$		9.86**		10.63**	128,000	0
19		–	122-124	$C_{14}H_{11}O_5N$		5.22*		5.13*	128,000	4,000
20		–	209-210	$C_{14}H_{13}O_3N$		5.52*		5.76*	0	0
21 .		–	172-175	$C_{13}H_{14}O_2N_2$		11.80*		12.17*	32,000	2,000

According to the literature data, 4,4'-dihydroxydiphenylmethane is obtained together with 2,4'-dihydroxydiphenylmethane by interaction of phenol and formaldehyde in presence of dilute hydrochloric acid [2]. The total yield of the two isomers under various experimental conditions is 12-15%. Fractionation of the isomers is effected by distillation in vacuum followed by fractional crystallization from large amounts of water. We obtained a mixture of 4,4'- and 2,4'-dihydroxydiphenylmethanes by condensing two moles of phenol with one mole of formaldehyde in presence of dilute hydrochloric acid at room temperature. The isomers were separated by fractional precipitation of their methanol solution with water; in this way the over-all yield was raised to 21%. 2,4-Dihydroxydiphenylmethane was obtained, as described by Klarmann [3], by reaction of resorcinol with benzyl chloride in presence of aluminum chloride in nitrobenzene solution. Fractionation of the reaction products was effected by us by direct distillation in vacuum instead of by the laborious chemical treatment proposed by Klarmann.

Ethers of diphydroxydiphenylmethanes were synthesized by two methods: by heating molar amounts of the respective hydroxy- or dihydroxydiphenylmethane, alkyl halide and KOH in alcoholic solution; or by heating sodium benzylphenolates with the molecular equivalent of alkyl halide in toluene solution.

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* Analytical results for nitrogen

** Analytical results for sulfur

*** Analytical results for chlorine

For the synthesis of the carbamino ether of 3-chloro-4 hydroxydiphenylmethane (prep. No. 17), 4-hydroxydiphenylmethane was transformed with the help of sulfuryl chloride into 3-chloro-4-hydroxydiphenylmethane [4], successive reaction of which with carbonyl chloride and ammonia gave the corresponding carbamino ether [5]. Formylation of 2,4-dihydroxydiphenylmethane with formanilide [6] leads to 2,4-dihydroxy-5-formyldiphenylmethane, which by the usual procedure was transformed into the thiosemicarbazone (prep. no. 18).

According to the literature data, 3-carboxy-4-hydroxydiphenylmethane is formed by treating sodium benzylphenate with carbon dioxide [7]. We synthesized this compound by condensing benzyl chloride with methyl salicylate in presence of zinc chloride; the resultant 3-carbomethoxy-4 hydroxydiphenylmethane was saponified to 3-carboxy-4-hydroxydiphenylmethane. Nitration of the latter compound gave 3-carboxy-4-hydroxy-5-nitrodiphenylmethane (prep. No. 19), which was further subjected to reduction to 3-carboxy 4-hydroxy-5-aminodiphenylmethane (prep. No. 20).

Reduction of 3,3' dinitro-4,4'-dihydroxydiphenylmethane, synthesized by the patented procedure [8], gave 3,3'-diamino-4,4'-dihydroxydiphenylmethane (prep. No. 21).

The majority of the prepared compounds showed considerable activity *in vitro* toward *Mycobacterium tuberculosis* and *Trichophiton gypseum*. Negative results were obtained, however, in tests *in vivo*.

EXPERIMENTAL

4,4'- and 2,4'-dihydroxydiphenylmethane. A mixture of 200 g phenol, 86 g 37% aqueous formaldehyde, 317 ml concentrated HCl and 1270 ml water was mixed at room temperature for 48 hours. A frothy mass formed in the flask and consisted of a mixture of solid particles and oily drops. On filtration a large proportion of the oil goes into the filtrate and oily crystals remain on the filter. The latter are dissolved in cold methyl alcohol and water is added until turbidity appears. The crystals are drained at the pump and dried. M.p. 159-160°. Yield 25.6 g or 12% of the theoretical.

The filtrate after collection of the 4,4'-dihydroxydiphenylmethane is diluted with water until an oily layer is formed; this is separated and added to the main bulk of oil obtained from the mother liquor when filtering the reaction mass. The oily liquid is dissolved in ether, the ethereal solution is washed with water and dried with sodium sulfate. After removal of the ether, the residue is distilled in vacuum. Phenol first comes over and is followed by 2,4'-dihydroxydiphenylmethane. B.p. 204-208° at 6 mm. The substance quickly crystallizes. After recrystallization from water the m.p. is 114-116°. Yield 19.3 g or 9% of the theoretical.

Scheiber gives m.p. 160° for 4,4'-dihydroxydiphenylmethane and 115-116° for 2,4' dihydroxydiphenylmethane [2].

2,4-Dihydroxydiphenylmethane. To a cooled solution of 60 g resorcinol in 300 ml nitrobenzene is added a solution of 36 g benzyl chloride and 36 g aluminum chloride. The reaction mass is heatedat 70° for 2 hours, cooled, and poured onto ice. The aqueous layer is separated from the nitrobenzene layer and extracted with ether; the ethereal extract is combined with the nitrobenzene solution which is washed with water, then with saturated sodium carbonate solution, and dried with sodium sulfate. The ether is driven off and the residue distilled in vacuum. Nitrobenzene first comes over, followed by unreacted resorcinol, and finally by 2,4-dihydroxydiphenylmethane inthe form of a yellow, viscous liquid. After two distillations, the 2,4-dihydroxydiphenylmethane slowly crystallizes on standing. Crystallization is more easily effected by dissolving the distilled material in hot benzene and gradually cooling the benzene solution. Colorless crystals, m.p. 74-76°. Yield 25.4 g or 44.6% of the theoretical. The literature [3] reports a yield of 50%, m.p. 76°.

Propyl ether of 4-hydroxydiphenylmethane. To a solution of 1.54 g KOH in 20 ml absolute alcohol is added 5 g 4-hydroxydiphenylmethane and 3.34 g n-propyl bromide. The reaction mass is heated at the boil for 3 hours, then cooled and treated with 60 ml water. The oily layer is separated; the aqueous layer is extracted with ether; the ethereal extract is combined with the separated oil which is dried with sodium sulfate. The ether is driven off and the residue distilled in vacuum. Yield 5.24 g or 85.5% of the theoretical. Colorless liquid, readily soluble in organic solvents, insoluble in water.

Octyl ether of 4-hydroxydiphenylmethane. To an alcoholic solution of sodium ethylate, prepared from 0.88 g sodium and 18 ml absolute alcohol, is added 7 g 4-hydroxydiphenylmethane. The alcohol is distilled off in vacuum. To the solid sodium benzylphenate is added 24 ml dry toluene and 7.35 g n-octyl bromide. The mixture is heated at the boil for 8 hours. The cooled reaction mixture is treated with 50 ml water; the toluene layer is separated and dried with sodium sulfate. The toluene is driven off and the residue distilled in vacuum. On standing,the compound crystallizes. White crystalline powder, readily soluble in organic solvents, insoluble in water. Yield 7.83 g or 69.5% of the theoretical.

Carbamino ether of 3-chloro-4-hydroxydiphenylmethane. To a solution of 40 g carbonyl chloride in 230 ml dry benzene is added, with stirring and cooling, a solution of 58 g 3-chloro-4-hydroxydiphenylmethane [4] in a mixture of 30 ml benzene and 40 g dimethylaniline. The reaction mass is mixed for 3 hours at room temperature. Addition is then made of 10 ml conc. hydrochloric acid with good stirring. The benzene layer is collected and washed with water and slowly run into 80 ml 25% aqueous ammonia, cooled with ice. The reaction mass is kept for 15 hours at room temperature. The precipitated carbamino ether of 3-chloro-4-hydroxydiphenylmethane is filtered, washed with water and dried. After recrystallization from alcohol it has m.p. 141-142°. A white crystalline powder, readily soluble in alcohol, ether, acetone, insoluble in water. Yield 32 g or 37.5% of the theoretical.

2,4-Dihydroxy-5-formyldiphenylmethane. To a cooled solution of 4 g 2,4-dihydroxydiphenylmethane and 2.4 g formanilide in 20 ml absolute ether is added 1 g phosphorus oxychloride. The reaction mass is brought to the boil, gradually cooled and left at room temperature for 12 hours. Addition is then made of 100 ml 3% sodium hydroxide solution and the aniline is distilled off. The residue is acidified with 10% sulfuric acid and extracted with ether. The ethereal solution is dried with sodium sulfate. From the brown, viscous residue (after removal of the ether) a thiosemicarbazone is prepared by the usual method and has m.p. 207-208°. (After recrystallization from alcohol). Orange-yellow crystalline powder, readily soluble in acetone and alcohol, insoluble in water.

3-Carbomethoxy-4-hydroxydiphenylmethane. 12.7 g benzyl chloride, 30.4 g methyl salicylate and 2.5 g zinc chloride are heated to 65° at which temperature hydrogen chloride begins to come off violently. When the evolution of HCl has slowed down, the reaction mass is heated on a boiling water bath for 3 hours. The cooled reaction mass is poured into 100 ml water. The oily layer is collected and the aqueous layer extracted with ether; the ethereal extracts are added to the oil which is washed with water and dried with sodium sulfate. The ether is driven off and the residue distilled in vacuum. A fraction boiling between 170 and 190° at 3 mm is collected. It crystallizes on standing. After recrystallization from alcohol, 9.2 g 3-carbomethoxy-4-hydroxydiphenylmethane with m.p. 76-77° is obtained. White crystals, readily soluble in the common organic solvents, insoluble in water. Yield 38% of the theoretical.

3-Carboxy-4-hydroxydiphenylmethane. 5 g 3-carbomethoxy-4-hydroxydiphenylmethane and 15 ml 10% NaOH solution are heated at the boil for 2½ hours. The cooled reaction mass is treated with 17% hydrochloric acid until acid to Congo. The precipitated white crystals are drained at the pump, washed with water and dried. M.p. 139°. Yield 4.6 g or 98% of the theoretical. The literature [7] reports m.p. 139-140°.

3-Carboxy-4-hydroxy-5-nitrodiphenylmethane. To a solution of 5 g 3-carboxy-4-hydroxydiphenylmethane in 50 ml acetic acid is added 1 ml nitrous acid (s.g. 1.51) at 8-10°. The reaction mass is mixed for 3 hours and then poured into cold water. The precipitate is filtered, washed with water and dried in the air. Yellow crystalline powder, readily soluble in alcohol, insoluble in ether or water. M.p. 122-124° (from aqueous alcohol). Yield 5.1 g or 85% of the theoretical.

3-Carboxy-4-hydroxy-5-aminodiphenylmethane. A solution of 3 g 3-carboxy-4-hydroxy-5-nitrodiphenylmethane in 30 ml alcohol is reduced in presence of 3 g skeletal nickel catalyst at room temperature. At the conclusion of hydrogen absorption, the catalyst is filtered off, the alcoholic solution is evaporated to dryness in vacuum and the residue is recrystallized from aqueous alcohol. White powder, darkening in the air, readily soluble in alcohol, poorly soluble in water, ether and acetone. M.p. 209-210°. Yield 1.26 g or 47.2% of the theoretical.

3,3'-Diamino-4,4'-dihydroxydiphenylmethane. A solution of 10 g 3,3'-dinitro-4,4'-dihydroxydiphenylmethane in 200 ml alcohol is reduced in presence of 10 g skeletal nickel catalyst at room temperature. After absorption of the theoretical amount of hydrogen, the catalyst is filtered off and the alcoholic solution evaporated in vacuum. The product is purified by conversion to the hydrochloride and by regeneration with saturated sodium bicarbonate solution. A light-brown, crystalline powder, readily soluble in alcohol and acetone, poorly in ether, insoluble in water. M.p. 172-175°. Yield 6.25 g or 78.6% of the theoretical.

SUMMARY

1. The methods described in the literature for preparation of 4,4'- and 2,4'-dihydroxydiphenylmethanes have been simplified.

2. A series of new derivatives of hydroxy- and dihydroxydiphenylmethanes have been synthesized and tested for chemotherapeutic activity.

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SYNTHESIS OF HYDROCARBONS OF THE 1,2-BENZANTHRACENE SERIES

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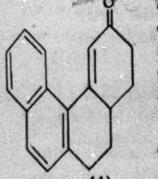
It was previously shown [1] that α-(3-chlorocrotyl)-γ-(2-naphthyl)-butyric acid undergoes intramolecular acylation in the 1-position when treated with sulfuric acid; this is followed by a second cyclization of the intermediate 1,5-diketone with formation of a tetracyclic ketone with the carbon skeleton of 3,4-benzophenanthrene (A).

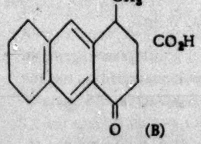


(A)

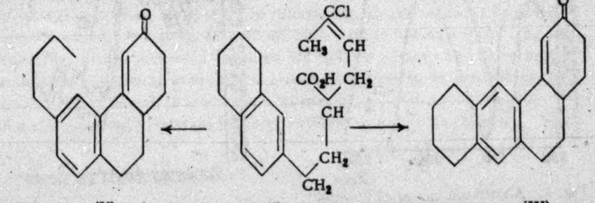
γ-(2-Naphthyl)-butyric acids which are alkylated in the side chain and in the naphthalene nucleus are also generally cyclized in the 1-position, but in exceptional cases the alkyl groups occupying certain positions in the nucleus (for example the 8-position) alter the direction of cyclization of naphthalenebutyric acids [2]. Saturation of one of the rings of the naphthalene nucleus brings about a similar effect; cyclization of γ-(5,6,7,8-tetrahydro-2-naphthyl)-butyryl chloride by heating under reduced pressure leads to a mixture of approximately equal parts of ketones of the phenanthrene and anthracene series [3].

On cyclization of the same acid with the help of conc. sulfuric acid, other authors [4] obtained a ketone of the anthracene series as the sole product. Similar observations were made in an attempt to prepare 1-methyl-2-carboxy-4-keto-octahydrophenanthrene [5]; contrary to the author's expectation, treatment of the initial anhydride of α-(5,6,7,8-tetrahydro-2-naphthyl)-ethylsuccinic acid with aluminum chloride in nitrobenzene led to its complete cyclization into the corresponding anthracene derivative (B). Consequently, in these cases tetralylbutyric acids, like the nuclear-substituted phenylbutyric acids, are acylated in the p-position with respect to the original substituent.

On the basis of the cited data, it was to be expected that sulfuric acid hydrolysis and cyclization of α-(3-chlorocrotyl)-γ-(5,6,7,8-tetrahydro-2-naphthyl)-butyric acid (I) would yield not the 3,4-benzophenanthrene derivative (II) but the isomeric compound of the 1,2-benzanthracene series (III):

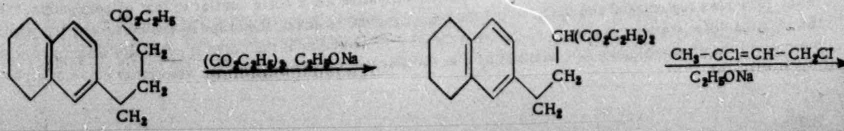


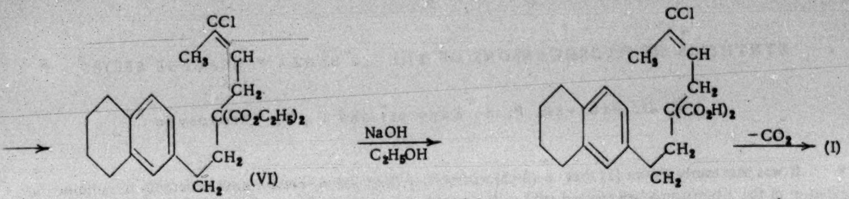
(B)



(II) (I) (III)

1,2-Benzanthracene and its homologs constitute, in respect their biological properties, a most interesting series of tetracyclic aromatic hydrocarbons with four condensed rings. At the present time several synthetic metho supplementing one another, are known and extensively employed for the synthesis of benzanthracene homologs; a large number of these have been developed by B. M. Mikhailov and co-workers [6]. Since the above scheme could prove convenient as a new route to hydrocarbons of the benzanthracene series, it was decided to attempt the synthesis of acid (I) and to study the product of its sulfuric acid hydrolysis and cyclization with the aim of preparing homologs of benzanthracene. γ-(5,6,7,8-Tetrahydro-2-naphthyl)-butyric acid, prepared by the literature method of condensation of tetralin with succinic anhydride followed by reduction of the keto-acid, was converted into the monosubstituted malonic ester (V) by condensation of its ethyl ester (IV) with diethyl oxalate and by thermal decarboxylation of the condensation product. Acid (I) was prepared from the substituted malonic ester (V) and 1,3-dichloro-2-butene by a three-step synthesis.





The product of interaction of acid (I) with sulfuric acid (s.g. 1.78) at 70-85°, obtained in 52.8% yield and forming a dinitrophenylhydrazone, corresponded in composition to formulas (II) and (III).

The ultraviolet absorption spectrum of the prepared ketone was plotted in the conditions described in the preceding paper [7]. The shape of the absorption curve of the ketone resembles that of benzylideneacetone [8] (Fig. 1), as was to be expected since a tetracyclic ketone, independently of whether it contains the cyclic skeleton of 1,2-benzanthracene (III) or 3,4-benzphenanthrene (II), must contain the conjugated double bond system of benzylideneacetone.

The maximum on the absorption curve of the tetracyclic ketone is shifted by approximately 30 mμ in the long-wave direction in comparison with the maximum of the benzylideneacetone curve. This circumstance, taking into consideration the existing literature data [8], must be explained by the fact that the investigated ketone is a β-substituted derivative of benzylideneacetone.

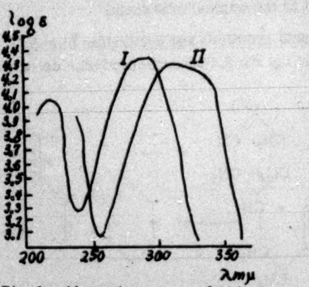


Fig. 1. Absorption curves of 2'-keto-decahydro-1,2-benzanthracene (II) and of benzylideneacetone (I) [8] in ethyl alcohol.

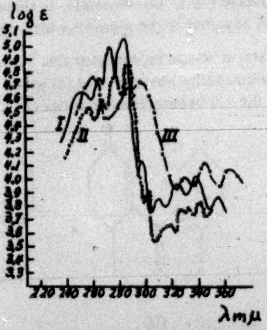


Fig. 2. Absorption curves of 1,2-benzanthracene (I), 2'-methylbenzanthracene (II) and 2'-phenylbenzanthracene (III) in ethyl alcohol.

The structure of the ketone was established by its dehydrogenation with platinized carbon; the main product of dehydrogenation was 1,2-benzanthracene (VIII) formed in a yield of 66.4% and identified as the picrate. A small amount of 2'-hydroxy-1,2-benzanthracene (IX) was also formed.

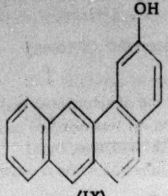
Organomagnesium compounds add on to the α,β-unsaturated ketone (III) exclusively in the 1,2-position, evidently due to the difficulty of addition of the alkyl group to the completely substituted and consequently difficultly accessible (from the steric aspect) β-carbon atom C_1. Reaction of the ketone with the appropriate Grignard reagents followed by dehydrogenation gave the previously described [9] 2'-methyl-1,2-benzanthracene and 2'-phenyl-1,2-benzanthracene (X) (the latter synthesized here for the first time).

These hydrocarbons were characterized in the form of picrates and maleic anhydride adducts.

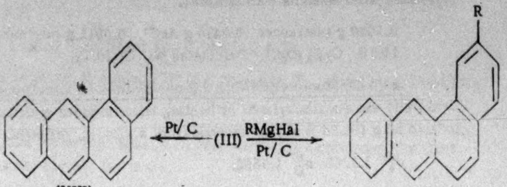
The general shape and the position of the maxima of the ultraviolet absorption curves of benzanthracene and its 2'-methyl homolog (Fig. 2) are close to those of the parent hydrocarbon obtained by other authors [10].

In contrast to these hydrocarbons, the 2'-phenyl derivative has a curve similar to that of benzanthracene only in the long-wave region (310-360 mμ). In the short-wave region, however, the shape of the curve and the position of the maxima differ sharply from those of the other curves. This section of the curve is evidently associated with the presence of the diphenyl group as evidenced by the similarity of this section with the absorption curve of diphenyl

[11]. The maxima on this section of the curve, by comparison with the absorption curve of diphenyl, are sharply displaced in the long-wave direction, probably due to the threefold annelation of the diphenyl molecule [12].



(IX)



(VIII) (X)

EXPERIMENTAL

The initial β-(5,6,7,8-tetrahydro-2-naphthoyl)-propionic acid was prepared in 88.5% yield by condensation of tetralin with succinic anhydride [13]. Reduction of the keto acid with amalgamated zinc and hydrochloric acid [14] gave a 78% yield of the acid which distilled at 195-205° (6 mm) and crystallized completely in the receiver; m.p. 44-47°.

Ethyl γ-(5,6,7,8-tetrahydro-2-naphthyl)-butyrate (IV). A mixture of 175 g acid, 400 g absolute alcohol and 7.5 g conc. sulfuric acid was boiled under a reflux condenser for 7 hours; the greater part of the alcohol was then distilled off, 400 ml water was added and the product extracted with ether; the ethereal solution was washed with sodium carbonate solution, then with water and dried with anhydrous sodium sulfate. Removal of the solvent left 182 g (92.2% of the theoretical amount) of a colorless liquid with b.p. 160-165° at 4 mm.

d_4^{22} 1.0381; n_D^{22} 1.5348.

0.1054 g substance: 0.3090 g CO_2; 0.0862 g H_2O. 0.1016 g substance: 0.2911 g CO_2; 0.0816 g H_2O. Found %: C 78.40, 78.14; H 9.08, 8.92. $C_{16}H_{22}O_2$. Calculated %: C 78.05; H 8.94.

β-(5,6,7,8-Tetrahydro-2-naphthyl)-ethylmalonic ester (V). To a weighed amount of sodium alcoholate, prepared from 6.1 g sodium and 12.6 g absolute alcohol in 200 ml dry ether, was added a solution of 57 g diethyl oxalate in 50 ml absolute ether. After standing for an hour, gradual addition was made to the light-yellow solution, with stirring, of a solution of 64 g of ester (IV) in 50 ml dry ether. The mixture was gently boiled for 24 hours, after which it was cooled and decomposed with dilute sulfuric acid (15 ml conc. acid in 200 ml water). The ethereal solution of the reaction product was washed with water and dried with sodium sulfate. The oil remaining after removal of the ether was decarboxylated by heating in vacuum at a residual pressure of the order of 10-12 mm until the frothing due to evolution of carbon monoxide had ceased. After driving off the excess of ethyl oxalate and unreacted ester (IV), 55 g of a colorless, viscous oil with b.p. 194-195° at 2 mm was collected. Yield 55 g (66.4% of the theoretical).

d_4^{22} 1.0737; n_D^{22} 1.5230.

0.1027 g substance: 0.2710 g CO_2; 0.0758 g H_2O. Found %: C 71.97; H 8.20. $C_{19}H_{26}O_4$. Calculated %: C 71.69; H 8.17.

[β-(5,6,7,8-Tetrahydro-2-naphthyl)-ethyl-(3-chloro)-crotyl]-malonic ester (VI). To a solution of sodium alcoholate, prepared from 7.45 g sodium and 85 g absolute alcohol, was added 100 g of the mono-substituted malonic ester (V). After heating on the water bath for half an hour, the solution was cooled and gradual addition was made (with shaking) of 50 g freshly distilled 1,3-dichloro-2-butene. The mixture was refluxed for 5 hours; part of the alcohol was then distilled off; the residue was acidified, the product was dissolved in ether and the solution washed with water and dried with sodium sulfate. Distillation in vacuum gave 95.8 g (74.9% of the theoretical) of a thick, light-greenish liquid with b.p. 226-228° at 2 mm.

d_4^{23} 1.1080; n_D^{23} 1.5281.

0.1042 g substance: 0.0349 g AgCl. 0.1054 g substance: 0.0437 g AgCl. Found %: Cl 8.34, 8.59. $C_{23}H_{31}O_4Cl$. Calculated %: Cl 8.73.

[β-(5,6,7,8-Tetrahydro-2-naphthyl)-ethyl-(3-chloro)-crotyl]-malonic acid (VII). A mixture of 106 g ester (VI), 32 g NaOH and 440 g 90% alcohol was refluxed for 4 hours, after which 300 ml water was run in and the alcohol completely driven off. Acidification of the cooled solution with hydrochloric acid brought down a heavy, yellowish oil. This was dissolved in ether and the solution washed and dried with sodium sulfate. After removal of the ether, the residue crystallized completely. Yield 85 g (93.0% of the theoretical) of colorless crystals with m.p. 137° after washing with benzene.

0.1020 g substance: 0.0430 g AgCl. 0.0911 g substance: 0.0374 g AgCl. Found %: Cl 10.43, 10.19. $C_{19}H_{23}O_4Cl$. Calculated %: Cl 10.12.

α-(3-Chlorocrotyl)-γ-(5,6,7,8-tetrahydro-2-naphthyl)-butyric acid (I). 65 g of the di-substituted malonic acid (VII) was decarboxylated by heating under reduced pressure. The resultant viscous oil was distilled in vacuum to give 53 g (93.24% of the theoretical) of a viscous, yellowish liquid with b.p. 216-218° at 1 mm.

d_4^{25} 1.1303; n_D^{25} 1.5598.

0.1054 g substance: 0.0493 g AgCl. 0.1021 g substance: 0.494 g AgCl. Found %: Cl 11.57, 11.97. $C_{18}H_{23}O_2Cl$. Calculated %:

2'-Keto-2,3,4,5,6,7,8,2',3',4'-decahydro-1,2-benzanthracene (III). To 15 ml sulfuric acid (s.g. 1.78) at room temperature was gradually added 3 g of the substituted butyric acid (I). Progressive addition was accompanied by deepening of the yellow color. Heating of the mixture on a water bath in a carbon dioxide stream initiated copious evolution of hydrochloric acid. The temperature was held at 70-80° for 3 hours until the substance had dissolved completely and hydrogen chloride had ceased to come off. The dark-red solution was then left overnight. Stirring of the reaction mixture with iced water caused separation of a viscous oil which crystallized completely on trituration. The substance was triturated with alkali solution, filtered, washed with water and dried. Recrystallization from alcohol gave 1.3 g (52.8% of the theoretical) of colorless crystals with m.p. 92-94°.

0.1006 g substance: 0.3155 g CO_2; 0.0732 g H_2O. 0.1004 g substance: 0.3152 g CO_2; 0.0730 g H_2O. Found %: C 85.53, 85.62; H 8.08, 8.07. $C_{18}H_{20}O$. Calculated %: C 85.71; H 7.93.

The bright-red 2,4-dinitrophenylhydrazone melted at 223-224° after recrystallization from a mixture of chloroform and alcohol. In spite of repeated recrystallization, the nitrogen content found for the substance was lower than the calculated value.

0.1026 g substance: 12.2 ml N_2 (28°, 676 mm). 0.1020 g substance: 12.2 ml N_2 (26°, 677 mm). Found %: N 12.10, 12.16. $C_{24}H_{24}O_4N_4$. Calculated %: N 12.98.

1,2-Benzanthracene (VIII). 3 g ketone (III) was dehydrogenated by heating with 1.2 g platinized carbon in a stream of carbon dioxide at 300-320° until hydrogen bubbles ceased to come off (about half an hour). The product was extracted with benzene; the benzene solution was washed with alkali, then with water and dried with sodium sulfate. Acidification of the washed alkali solution led to separation of a small amount of acid dehydrogenation product. The crystalline residue after removal of the benzene was obtained in the form of light-green leaflets with m.p. 159° after recrystallization from alcohol (boiled with carbon). The literature [15] reports m.p. 159-160°. Yield 1.8 g (66.4% of the theoretical).

0.1004 g substance: 0.3478 g CO_2; 0.0490 g H_2O. Found %: C 94.67; H 5.42. $C_{18}H_{12}$. Calculated %: C 94.73; H 5.26.

The dark-red picrate, isolated from benzene solution, had m.p. 133-134°.

0.1052 g substance: 9.2 ml N_2 (29°, 674 mm). Found %: N 8.79. $C_{24}H_{15}O_7N_3$. Calculated %: N 9.19.

2'-Hydroxy-1,2-benzanthracene (IX). The acid dehydrogenation product collected from three experiments on dehydrogenation of ketone (III) weighed 0.35 g after recrystallization from alcohol and was obtained in the form of light-green crystals with m.p. 186-188°.

0.1002 g substance: 0.3258 g CO_2; 0.0480 g H_2O. Found %: C 88.67; H 5.32. $C_{18}H_{12}O$. Calculated %: C 88.52; H 4.92.

2'-Methyl-1,2-benzanthracene (X, $R=CH_3$). To the Grignard solution prepared from 4 g Mg and 25 g methyl iodide was added, with stirring, an ethereal solution of 10 g ketone (III). After boiling for 2 hours, the cooled mixture was decomposed with dilute hydrochloride acid. The product was dissolved in ether, and the solution was washed with water and dried with sodium sulfate. Removal of the ether left 7.5 g yellow oil. 1.8 g of this oil was dehydrogenated with 0.3 g platinized carbon by heating for half an hour at 300-320° in a carbon dioxide atmosphere. The product was extracted with benzene and the solution washed with water and dried. The oil remaining after the benzene had been removed was dissolved in alcohol; slow evaporation of the latter left crystals with m.p. 142°. A second recrystallization from alcohol (boiling with carbon) gave 0.9 g (55.2% of the theoretical, calculated on the intermediately formed oil) of colorless leaflets with m.p. 148°. The literature [9] reports m.p. 148-149° for 2'-methyl-1,2-benzanthracene.

Found %: C 94.07, 94.10; H 6.21, 6.19. $C_{19}H_{14}$. Calculated %: C 94.21; H 5.79.

The brick-red picrate, recrystallized from benzene, had m.p. 177° (the literature [9] reports m.p. 178-179°).

Found %: N 8.71. $C_{25}H_{17}O_7N_3$. Calculated %: N 8.91.

Like the picrate of benzanthracene itself, the picrates of benzanthracene homologs decompose into their components when attempts to recrystallize them from alcohol are made.

2'-Methyl-9,10-dihydro-1,2-benzanthracene-9,10-endo-α,β-succinic anhydride. A solution of 0.5 g 2'-methylbenzanthracene and 5 g freshly distilled maleic anhydride in 10 ml dry toluene are refluxed for 4 hours. The adduct which separated on cooling is filtered, washed several times with small portions of water, dried and recrystallized from benzene. M.p. 234-235°.

0.1049 g substance: 0.3115 g CO_2; 0.0492 g H_2O. Found %: C 80.98; H 5.21. $C_{23}H_{16}O_3$. Calculated %: C 81.14; H 4.74.

2'-Phenyl-1,2-benzanthracene (X, R = C_6H_5). Reaction of Grignard reagent, prepared from 3 g Mg and 20 g bromobenzene, with 10 g ketone (III) gave 9 g oily product. Dehydrogenation of 3.5 g of this oil with platinized carbon (0.6 g) and recrystallization from alcohol (boiling with carbon) gave 2.14 g (70% of the theoretical, calculated on the intermediately formed oil) of colorless crystals with m.p. 145°.

0.0574 g substance: 0.2000 g CO_2; 0.0284 g H_2O. Found %: C 95.02; H 5.49. $C_{24}H_{16}$. Calculated %: 94.73; H 5.26.

The picrate, prepared from benzene in the form of acicular crystals with a bright-red color, had m.p. 159-160°.

0.1037 g substance: 8.2 ml N_2 (25°, 676 mm). Found %: N 8.03. $C_{30}H_{19}O_7N_3$. Calculated %: N 7.88.

2'-Phenyl-9,10-dihydro-1,2-benzanthracene-9,10-endo-α,β-succinic acid. A solution of 5 g maleic anhydride in 12 ml dry toluene was boiled with 0.56 g hydrocarbon (X, R = C_6H_5) for 4 hours; the precipitate was filtered and thoroughly boiled several times with dilute sodium hydroxide solution. Acidification of the filtered alkaline solution brought down a white precipitate. The dried compound had m.p. 277-278°.

0.0716 g substance: 0.2100 g CO_2; 0.0350 g H_2O. Found %: C 79.98; H 5.43. $C_{28}H_{20}O_4$. Calculated %: C 79.97; H 4.89.

SUMMARY

1. It was found that α-(3-chlorocrotyl)-γ-(5,6,7,8-tetrahydro-2-naphthyl)-butyric acid, prepared from tetralin by a seven-step synthesis, undergoes hydrolysis and double cyclization when treated with sulfuric acid and forms a tetracyclic ketone with the carbon skeleton of 1,2-benzanthracene.

2. Dehydrogenation of the ketone and of the products of its interaction with Grignard reagents gave 1,2-benzanthracene and 2'-methyl- and 2'-phenyl-benzanthracenes.

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SYNTHESES IN THE 1,2-BENZANTHRACENE SERIES WITH THE AID OF LITHIUM REAGENTS

B. M. Mikhailov and T.K. Kozminskaya

In previous communications we described the application of organolithium compounds to the synthesis of derivatives of 1,2-benzanthracene [1] and 3,4'-ace-1,2-benzanthracene [2] with substituents in the 10-position. In the further development of this method of synthesis, which had proved extremely promising in the polycyclic series [3,4], we studied the transformations of organolithium compounds of 1,2-benzanthracene with substituents in the 4' and 4', 10-positions.

Reaction of bromine with 4'-bromo-1,2-benzanthracene leads to smooth bromination in the 10-position. An attempt was made to verify the structure of the obtained dibromo compound by treatment with one equivalent of phenyllithium and by hydrogenation of the resultant lithium derivative. This gave 4'-bromo-1,2-benzanthracene (I), which only indicated the greater reactivity of the newly-introduced bromine atom but not its position. The problem of the structure of the dibromo compound was solved in the following way: the lithium compound (III), prepared from the dibromo compound and phenyllithium, was methylated with methyl iodide. The methylbromo derivative (IV) in turn was treated with an excess of n-butyllithium and the resultant methyllithium compound (V) was hydrogenated. This gave 10-methyl-1,2-benzanthracene (VI), thus providing proof that the dibromo compound was 4', 10-dibromo-1,2-benzanthracene (II)

Reaction of an excess of n-butyllithium with 4', 10-dibromo-1,2-benzanthracene leads to substitution of both atoms of bromine by the metal. The dilithium compound of 1,2-benzanthracene (VII) reacts with methyl iodide to form 4', 10-dimethyl-1,2-benzanthracene. We also investigated the possibility of utilization of 4'-bromo-1,2 benzanthracene (I) for synthesis of 4'-derivatives. It was found that the bromo compound (I) reacts smoothly with n-butyllithium and the resultant 4'-lithium-1,2-benzanthracene (IX) can be successfully used for synthesis of 1,2 benzanthracene derivatives. Carboxylation of 4'-lithium 1,2-benzanthracene results in a good yield of 1,2-benzanthracene-4'-carboxylic acid (X). Reaction of the organolithium compound with methyl iodide gives smooth conversion to 4'-methyl-1,2-benzanthracene (XI).

Bromination of 4'-methyl-1,2-benzanthracene takes place in the 10-position. The structure of the dibromo compound (XII) was confirmed by transformation into 4', 10-dimethyl-1,2-benzanthracene (VIII). This was effected by treating 10-bromo-4'-methyl-1,2-benzanthracene with excess n-butyllithium and subjecting the resultant 4'-methyl-10-lithium-1,2-benzanthracene (XIII) to the action of methyl iodide. The so-obtained hydrocarbon was compared with a specimen of 4', 10 dimethyl-1,2-benzanthracene synthesized from 4',10 dibromo-1,2-benzanthracene. 4'-Methyl-10-bromo-1,2-benzanthracene, via the lithium compound (XIII), is readily converted with ethyl iodide or ethylene oxide into, respectively, 4'-methyl-10-ethyl- or 4'-methyl-10- β-hydroxyethyl-1,2-benzanthracene (XV)

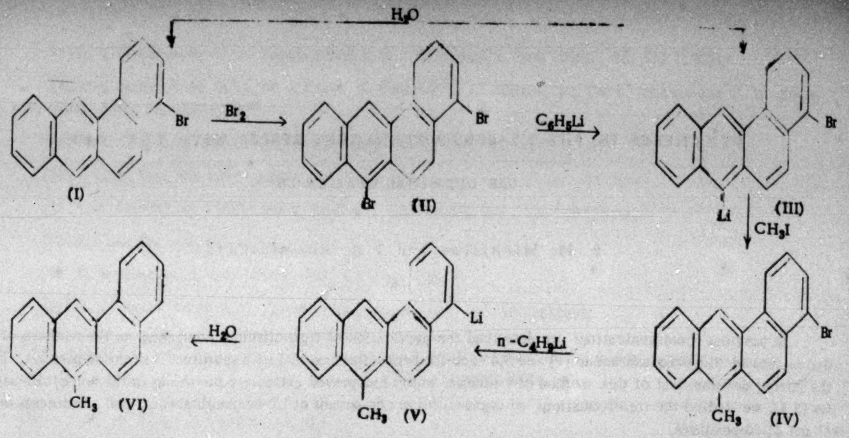
Carboxylation of 4'-methyl-1,2-benzanthryl-10-lithium gives smooth conversion to 4'-methyl-1,2-benzanthracene-10-carboxylic acid (XVI).

EXPERIMENTAL

4'-Bromo-1,2-benzanthracene (I). 1.5 g 4'-bromo-1,2-benzanthraquinone was dissolved in 150 ml glacial acetic acid, and to the solution was added 3 g tin chloride in 15 ml concentrated hydrocholoric acid. The reaction mixture was refluxed for an hour and poured into water the precipitate, quickly filtered at the pump, was washed with water. A small portion of the unrecrystallized 4'-bromo-1,2-benzanthrone was dried and analyzed.

5.437 mg substance: 13.031 mg CO_2; 1.768 mg H_2O. Found %: C 65.40; H 3.64; $C_{18}H_{11}OBr$. Calculated %: C 66.89; H 3.43.

The crude 4'-bromo-1,2-benzanthrone was quickly transferred to a flask and reduced by boiling for 1.5 hours with 15 ml of 2N NaOH and 1.5 g zinc dust. The cooled reaction mixture was filtered and the precipitate treated with dilute hydrochloric acid. The filtered and dried precipitate weighed 0.60 g and melted at 183-194°. Crystallization from acetic acid gave 0.41 g with m.p. 209-211° (30%). After one more recrystallization, 4'-bromo-1,2-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Br_2
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Br
(II)
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(III)
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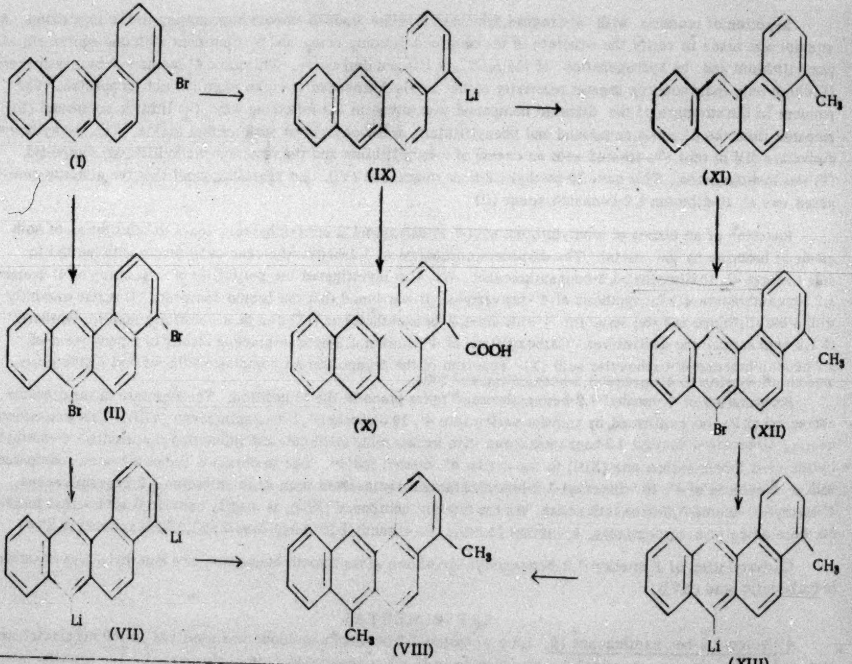
CH_3
(V)
CH_3
(IV)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(I)
(IX)
(XI)
Br
COOH
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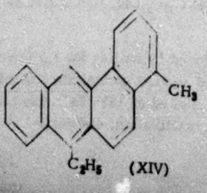
CH_3
Li
(VII)
CH_3
(VIII)
Li
(XIII)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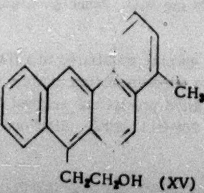
(XIV)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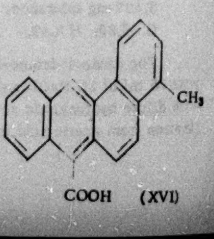
CH_2CH_2OH

(XV)


CH_3
COOH

(XVI)

benzanthracene melted at 210-211° in accord with the literature value [5].

From the combined mother liquors was isolated 0.32 g with m.p. 152-157.5° After crystallization from benzene this substance melted at 158-160° and did not give a depression in admixture with a specimen of 1,2-benzanthracene.

Reduction of the same quantity of 4'-bromo-1,2-benzanthracene in other conditions failed to raise the yield and to avoid reduction of 4'-bromo-1,2-benzanthracene to hydrocarbon. The alternative conditions were: use of 10 g Zn dust and 100 ml 2 N NaOH, 1 g Zn dust and 10 ml 2 N NaOH at the boil for 1 to 3 hours, activation of the zinc with copper sulfate, replacement of alkali by ammonia, and operation in presence of toluene.

Clemmensen reduction of the bromobenzanthrone led to negative results.

4', 10-Dibromo-1,2-benzanthracene (II). 1 g 4'-bromo-1,2-benzanthracene was dissolved by heating in 100 ml carbon tetrachloride. The hot solution was brominated by dropwise addition of 0.7 g bromine (20% excess) dissolved in 20 ml carbon tetrachloride. The reaction mixture, containing the precipitate, was heated to the boil. The precipitate dissolved completely. The reaction mixture was left overnight at room temperature. After driving off the solvent, the residue was crystallized from benzene to give 0.98 g greyish long, slender needles with m.p. 192-193.5° The yield of dibromo compound was 78.4% of the theoretical. After repeated crystallizations from benzene and isoamyl ether, 4',10-dibromo-1,2-benzanthracene melted at 194.5-195.5 °.

4.863 mg substance : 9.931 mg CO_2; 1.153 mg H_2O. Found %: C 55.73; H 2.65. $C_{18}H_{10}Br_2$. Calculated %: C 56.00; H 2.61.

10-Methyl-1,2-benzanthracene. 9 ml of an ethereal solution of phenyllithium (0.375 N), i.e., 1.3 moles, was run into a weighed amount (1 g) of dibromo compound (II) in 30 ml dry benzene. After brief shaking the precipitate of dibromo compound went into solution. 2 g methyl iodide was added to the reaction mixture. After 2 hours, the reaction products were poured into water; the solvent was driven off from the upper layer and the residue recrystallized from benzene. 0.62 g crystals with m.p. 178-181° was obtained. The m.p. rose to 182-183° after crystallization from ethyl acetate; the crystals under the microscope had the appearance of colorless rhombic platelets. The analysis accords with 4'-bromo-10-methyl-1,2-benzanthracene. Due to the solubility being similar to that of both the original bromo compound and 4',10-dimethyl-1,2-benzanthracene, the prepared compound cannot be easily freed from impurities.

5.068 mg substance: 12.866 mg CO_2; 1.755 mg H_2O. Found %: C 69.28; H 3.87. $C_{19}H_{13}Br$. Calculated %: C 71.05; H 4.08.

To 0.5 g of the prepared product, dissolved in 10 ml dry benzene, was added an ethereal solution of n-butyllithium prepared from 0.25 g n-butyl chloride. The reaction mixture was treated with water and the residue (following removal of solvent) was dissolved in ligroin and passed through alumina. 0.15 g substance was obtained with m.p. 134-137° (40%). After two crystallizations from ethanol it melted at 139-140° and did not give a depression with a specimen of 10-methyl-1,2-benzanthracene.

A solution in benzene-ether of the 4'-bromo-10-lithium-1,2-benzanthracene prepared by the above method from 0.5 g 4',10-dibromo-1,2-benzanthracene was poured into water. The layers were separated and the solvent was driven off from the upper layer. The residue was crystallized from benzene to give 0.16 g with m. p. 210-212°. A mixed test with a specimen of 4'-bromo-1,2-benzanthracene did not show a melting point depression. Yield 40% of the theoretical. A pure substance could not be isolated from the mother liquor.

4',10-Dimethyl-1,2-benzanthracene (VIII). The reaction between 0.5 g 4',10-dibromo-1,2-benzanthracene (dissolved in 40 ml dry benzene) and an ethereal solution of n-butyllithium (prepared from 0.5 g n-butyl chloride and 0.1 g metallic lithium) was continued for half an hour. After addition of 2.5 g methyl iodide over a period of 2 hours, the reaction mixture was treated with water and the solvent was driven off from the ether-benzene layer. The residue was crystallized from benzene and then from ethanol, giving 0.16 g crystals (48.4%) melting at 153-154°. The pure compound melts at 154-154.5°.

4.756 mg substance: 16.284 mg CO_2; 2.520 mg H_2O. 4.686 mg substance: 16.076 mg CO_2; 2.508 mg H_2O. Found %: C 93.64, 93.94; H 5.93, 5.98. $C_{20}H_{16}$. Calculated %: C 93.71; H 6.29.

1,2-Benzanthracene-4'-carboxylic acid (X). To an ethereal solution of n-butyllithium, prepared in the usual way from 0.25 g n-butyl chloride and 0.05 g lithium, was added a benzene solution of 0.5 g 4'-bromo-1,2-benzanthracene (40 ml). After 10 minutes, the reaction mixture was poured onto solid carbon dioxide and treated with water. Acidification of the filtered, alkaline aqueous layer gave 0.27 g light-yellow substance melting at 280-285° (yield 61.4% of the theretical) After crystallization from ethanol, 1,2-benzanthracene-4'-carboxylic acid melts at 286°.

4.769 mg substance: 14.632 mg CO_2; 2.032 mg H_2O. Found %: C 83.73; H 4.76. $C_{19}H_{12}O_2$. Calculated %: C 83.80; H 4.44.

A solid melting at 138-143° was isolated from the ether-benzene layer; it was impossible to isolate pure substances.

4'-Methyl-1,2-benzanthracene (XI). To an ether-benzene solution of 1,2-benzanthryl-4'-lithium, prepared from 2 g 4'-bromo-1,2-benzanthracene, was added an ethereal solution of 3 g methyl iodide. The color of the reaction mixture became light-yellow. At the expiration of 2 hours, water was added to the reaction mixture; the solvent was driven off from the ether-benzene layer and the residue was crystallized from benzene to give 1.13 g colorless platelets melting at 192-194°. Yield 72% of the theoretical. After a second crystallization from the same solvent, 4'-methyl-1,2-benzanthracene melted at 194-195° in agreement with the literature [6].

3.338 mg substance: 11.550 mg CO_2; 1.793 mg H_2O. Found %: C 94.42; H 6.01. $C_{19}H_{14}$. Calculated %: C 94.18; H 5.82.

4'-Methyl-10-bromo-1,2-benzanthracene (XII). 2 g 4'-methyl-1,2-benzanthracene was dissolved in 100 ml carbon bisulfide. Dropwise addition was slowly made to the solution of 1.62 g bromine (20% excess) dissolved in 40 ml carbon bisulfide. The reaction mixture was left overnight. The carbon bisulfide was driven off and the residue crystallized from benzene to give 1.9 g substance with m.p. 155-161°. After crystallization from benzene-ethanol, 1.7 g (60.4%) of substance with m.p. 158-162° was obtained. Recrystallization of the 4'-methyl-10-bromo-1,2-benzanthracene from ethyl acetate raised the m.p. to 162-164°.

6.112 mg substance: 15.924 mg CO_2; 2.284 mg H_2O. Found %: C 71.10; H 4.18. $C_{19}H_{13}Br$. Calculated %: C 71.04; H 4.07.

4',10-Dimethyl-1,2-benzanthracene from 4'-methyl-10-bromo-1,2-benzanthracene 0.75 g 4'-methyl-10-bromo-1,2-benzanthracene, dissolved in 22 ml dry benzene, was added to an ethereal solution of n-butyllithium prepared from 0.4 g n-butyl chloride. After 15 minutes an ethereal solution of 1.2 g methyl iodide was run into the brown-colored reaction mixture. Slight heat was developed and the reaction mixture gradually became lighter in color. After two hours the mass was worked up in the usual manner and the solid recovered from the ether-benzene layer was crystallized from benzene and ethanol to give 0.25 g of white, fluffy needles melting at 153.5-154.5°. The yield was 62.5 % of the theoretical. The substance does not give a depression of m.p. with a specimen of 4',10-dimethyl-1,2-benzanthracene that we prepared by another route.

4'-Methyl-1,2-benzanthracene-10-carboxylic acid (XVI). After 10 minutes' reaction between a benzene solution of 0.5 g 4'-methyl-10-bromo-1,2-benzanthracene and an ethereal solution of n-butyllithium, the reaction mixture was carboxylated. The cloudy aqueous layer was made alkaline, heated to the boil, and filtered. From the acidified filtrate was isolated 0.38 g of an acid melting at 236-240°. Yield 85.4% of the theoretical.

4.465 mg substance: 13.69 mg CO_2; 2.119 mg H_2O. Found %: C 83.68; H 5.31. $C_{20}H_{14}O_2$. Calculated %: C 83.89; H 4.93.

From the ether-benzene layer was isolated only 0.06 g of an oily product.

4'-Methyl-10-ethyl-1,2-benzanthracene (XIV). In similar conditions isolation was effected of 0.14 g substance with m.p. 194-197° from 0.5 g 4'-methyl-10-bromo-1,2-benzanthracene. Yield 33.3% of the theoretical. After crystallization from benzene and from ethanol, 4'-methyl-10-ethyl-1,2-benzanthracene melted at 198-199°. Under the microscope it had the form of fine, colorless prisms.

6.71 mg substance: 23.00 mg CO_2; 4.01 mg H_2O. Found %: C 93.54; H 6.64. $C_{21}H_{18}$. Calculated %: C 93.29; H 6.71.

4'-Methyl-10-β-hydroxyethyl-1,2-benzanthracene (XV). Reaction of gaseous ethylene oxide with an ether-benzene solution of 4'-methyl-1,2-benzanthryl-10-lithium (prepared from 0.5 g dibromo compound) gave crystals melting at 157-160° (from benzene). Yield 84.1%. A second crystallization from ethanol gave 4'-methyl-10-β-hydroxyethyl-1,2-benzanthracene in the form of colorless, fluffy needles with m.p. 159-160.5°.

6.04 mg substance: 19.46 mg CO_2; 3.47 mg H_2O. Found %: C 87.92; H 6.43. Calculated %: C 88.07; H 6.34.

SUMMARY

1. 4'-Bromo- and 4'-methyl-1,2-benzanthracene undergo bromination in the 10-position.

2. 4'-Bromo- and 4'-methyl-10-bromo-1,2-benzanthracene are smoothly transformed into organolithium compounds applicable to the syntheses of the corresponding derivatives of 1,2-benzanthracene.

3. 4',10-Dibromo-1,2-benzanthracene when treated with excess of n-butyllithium forms 4',10-dilithium-1,2-benzanthracene, which is suitable for the synthesis of 4',10-disubstituted 1,2-benzanthracenes.

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** " " " " " 527.
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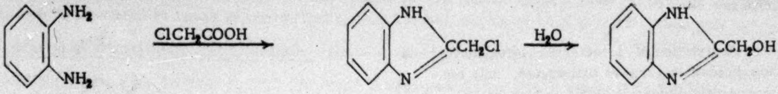
IMIDAZOLE DERIVATIVES

X. ACYLATION OF 2-HYDROXYMETHYLBENZIMIDAZOLE AND THE PRODUCTS OF ITS METHYLATION

N. A. Zakharova, B. A. Porai-Koshits, and L. S. Efros

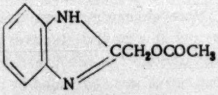
Many esters formed from aminoalchohols and organic acids are physiologically active compounds. Since benzimidazole derivatives frequently exhibit such properties, it seemed of interest to prepare a series of such esters, using a benzimidazole derivative as the aminoalcohol, namely 2-hydroxymethylbenzimidazole (I). We prepared this compound by the following route [1,2,3]:


NH₂
NH₂
ClCH₂COOH
NH
N
CCH₂Cl
H₂O
NH
N
CCH₂OH

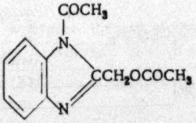
(I)

Acetylation of compound (I) with acetic anhydride in presence of anhydrous sodium acetate was carried out by Bystrzhitsky and Przhevorsky [4] who obtained a product which they assumed to be 2-acetoxymethylbenzimidazole (II).

In actuality, as we established in the present investigation, this compound is a diacetyl derivative and has the structure (III).

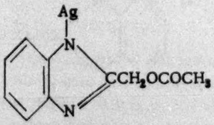

NH
N
CCH₂OCOCH₃

(II)

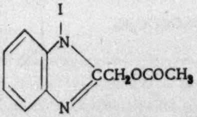

COCH₃
N
N
CCH₂OCOCH₃

(III)

The monoacetyl derivative (II) in which we are interested is obtained by performing the acylation reaction in slightly different conditions (omission of sodium acetate). The structure of the substance (II) that we prepared was confirmed by synthesis of its silver salt (IV) and iodoamine (V).

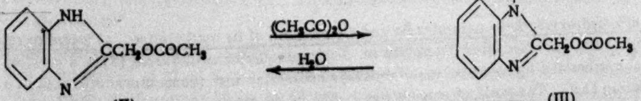

Ag
N
N
CCH₂OCOCH₃

(IV)


I
N
N
CCH₂OCOCH₃

(V)

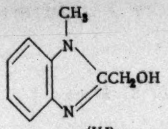
Further acylation of 2-acetoxymethylbenzimidazole leads to the diacetyl derivative (the reaction is reversible)


NH
N
CCH₂OCOCH₃
(CH₃CO)₂O
H₂O
COCH₃
N
N
CCH₂OCOCH₃

(II)

(III)

Consequently it is clear that in the acetylation of 2-hydroxymethylbenzimidazole, the reaction proceeds first at the hydroxyl group of this compound and subsequently a diacetyl compound is obtained in which the second radical of the organic acid is bound to one of the nitrogen atoms of the heterocycle. With the aim of obtaining conclusive evidence of the correctness of our theory of the course of the acetylation reaction and of confirming our suggested formula for the Bystrzhitsky product, we decided to acetylate 1-methyl-2-hydroxymethy benzimidazole (VI).

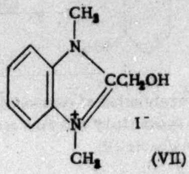


(VI)

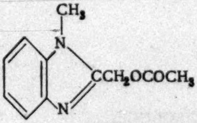
In this case acetylation could theoretically result in formation of only one compound — the product of substitution of the hydrogen of the hydroxy group. The inability of the prepared monoacetyl derivative to undergo further acetylation was indirectly confirmed by the fact that the second acetyl group enters the nitrogen heterocycle when the acetylation of monoacetoxymethylbenzimidazole is performed.

1-Methyl-2-hydroxybenzimidazole was prepared by the action of methyl iodide on 2-hydroxymethybenzimidazole in an alcoholic medium under pressure. Apart from this product, all the methylation experiments gave greater of lesser amounts of the methoiodide of 1-methyl-1-hydroxymethylbenzimidazole (VII). Raising the reaction temperature to above 120° results in a secondary reaction of reduction of the alcohol group. The separation of the components formed on methylation of 2-hydroxymethylbenzimidazole presented some experimental difficulties.

Acetylation of 1-methyl-2-hydroxymethylbenzimidazole gave, as anticipated, only the monoacetyl derivative (VIII), which is incapable of entering into further reaction with acetic anhydride.

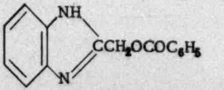


(VII)

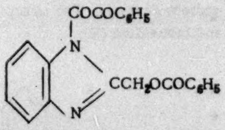


(VIII)

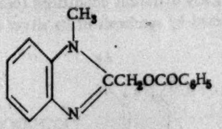
Benzoylation proceeds on precisely the same lines for 2-hydroxymethylbenzimidazole and for 1-methyl-2-hydroxymethylbenzimidazole. 2-Hydroxymethylbenzimidazole is benzoylated, like benzimidazole, in a pyridine medium [5] or a chlorobenzene medium. The reaction leads to a mixture of the mono- and dibenzoyl-derivatives (IX) and (X) and to an oily product whose structure was not established. The structure of the monobenzoyl derivative was confirmed by analysis and by the preparation of its silver salt whose structure is similar to that of (IV). Benzoylation of 1-methyl-2-hydroxymethylbenzimidazole gives a good yield of the corresponding ester (XI).



(IX)



(X)



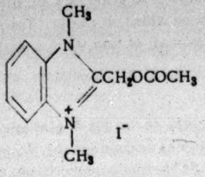
(XI)

The above-described reaction proceeded with considerably greater difficulty in the case of 1-methyl-2-hydroxymethylbenzimidazole methoiodide (VIII). In certain conditions it was possible to obtain and purify the derivative (XII), whereas we failed to obtain the benzoyl derivative and the starting material was recovered from the reaction mixture.

EXPERIMENTAL

1. Preparation of 2-hydroxymethylbenzimidazole and the products of its methylation. a) 2-Hydroxymethylbenzimidazole. Preparation was effected by hydrolysis of 2-chloromethylbenzimidazole [3] in a yield of 65-73.6%. The latter was synthesized by condensation of o-phenylenediamine with monochloracetic acid in a dilute hydrochloric acid medium [1,2]. The yield of product was 75-83% of the theoretical.

b) Methylation of 2-hydroxymethylbenzimidazole. A mixture of 5 g 2-hydroxymethylbenzimidazole, 5.6 ml methyl iodide and 5 ml absolute methyl aclohol is heated in a sealed tube at 70-90° for 5 hours. The precipitate (6.35 g) is filtered off; it consists of the hydroiodide of 1-methyl-2-hydroxymethylbenzimidazole and its methoiodide. It is dissolved in 10-15 ml water and, under ice cooling, addition is made of ammonia until the reaction is alkaline. A mixture of 1-methyl-2-hydroxymethylbenzimidazole (base) and the salt of the quaternary compound comes down. The precipitate is filtered and dried; weight 3.86 g. After drying, it is treated in 3 portions with 250 ml absolute benzene. The residue after treatment is 1.3 g of the methoiodide of 1-methyl-2-hydroxymethylbenzimidazole; the base goes into solution. The alcoholic filtrate from the reaction tube is evaporated to dryness, giving 2.9 g solid material. This is worked up as described above with water, ammonia and benzene; 0.9 g methoiodide remains undissolved.



(XII)

The benzene solutions are combined and the benzene is driven off to leave 1.8 g of 1-methyl-2-hydroxymethylbenzimidazole base. Two crystallizations from benzene give 1.2 g with m.p. 146-147° (yield 20.1% of the theoretical).

The ammoniacal filtrates are combined and evaporated to dryness; the residue is worked up with a small quantity of boiling absolute ethyl alcohol; on cooling, 0.8 g methoiodide is obtained. All the precipitates of quaternary base are combined and crystallized twice from absolute alcohol. 2.09 g of the methoiodide of 1-methyl-2-hydroxymethylbenzimidazole is obtained with m.p. 187-188° (20.35%). The mixture of salts of the tertiary and quaternary bases can also be separated by repeated crystallization from alcohol, but the yield of products is then very low.

1-Methyl-2-hydroxymethylbenzimidazole. White crystals with m.p. 146-147°.

0.1092 g substance: 16.6 ml N_2 (20°, 752 mm). 0.0985 g substance: 14.65 ml N_2 (21°, 759 ml). Found %: N 17.53, 1725 $C_9H_{10}ON_2$. Calculated %: N 17.28.

The hydrochloride is obtained by passing dry hydrogen chloride through a solution of the base in absolute alcohol and precipitating the salt with absolute ether. M.p. 189-190°.

0.2430 g substance: 0.1765 g AgCl. 0.2325 g substance: 0.1654 g AgCl. Found %: Cl 17.96, 17.60. $C_9H_{11}ON_2Cl$. Calculated %: Cl 17.85.

The hydroiodide has an unsharp melting point.

0.1032 g substance: 8.7 ml N_2 (19°, 760 mm). 0.1149 g substance: 9.45 ml N_2 (20°, 769 mm). 0.2244 g substance: 0.1795 g AgI. Found %: N 9.87, 9.70; I 43.24. $C_9H_{11}ON_2I$. Calculated %: N 9.66; I 43.75.

Methoiodide of 1-methyl-2-hydroxymethylbenzimidazole. Colorless or greenish lustrous needles with m.p. 187-188°.

0.1309 g substance: 10.9 ml N_2 (20°, 747 mm). 0.1183 g substance: 9.4 ml N_2 (21°, 770 mm). 0.2132 g substance: 0.1643 g AgI. 0.2726 g substance: 0.2093 g AgI. Found %: N 9.54, 9.34; I 41.66, 41.50. $C_{10}H_{13}ON_2I$. Calculated %: N 9.21; I 41.73.

Methylation of 2.4 g 2-hydroxymethyl benzimidazole base gave 4.4 g product which after crystallization from water or 10% ammonia gave 3.8 g methoiodide of 1,2-dimethylbenzimidazole with m.p. 258-259° [6].

Found %: I 44.22, 44.13. $C_{10}H_{13}N_2I$. Calculated %: I 44.05.

The same compound was synthesized from 2-methylbenzimidazole. In the above-described conditions, 2.6 g (0.02 mole) base of 2-methylbenzimidazole gives 3.85 g crude product which after two crystallizations gives 2.7 g lustrous needles with m.p. 257-258°. Both in properties and in outward appearance, this product was identical with the one described above. A mixed sample gave m.p. 258-259°.

2. Acetylation of 2-hydroxymethylbenzimidazole and of the products of its methylation. a) 2-Acetoxymethylbenzimidazole. 7 g (0.05 mole) 2-hydroxymethylbenzimidazole, 9.45 ml (0.1 mole) acetic anhydride and 10 ml glacial acetic acid are heated on a boiling water bath for 30-40 minutes; the solution is then evaporated to dryness, giving 8.95 g (98.7%) crude product. Two crystallizations from benzene or water give 6.3 g white prisms with m.p. 163-164°.

0.2044 g substance: 26.6 ml N_2 (22°, 756 mm). 0.1787 g substance: 23.4 ml N_2 (22°, 752 mm). 0.0261 g substance: 6.87 ml 0.02 N NaOH. 0.0302 g substance: 7.88 ml 0.02 N NaOH. Found %: N 14.98, 14.99; acetyl groups 22.65, 22.47. $C_{10}H_{10}O_2N_2$. Calculated %: N 14.73; acetyl groups 22.63.

The compound is poorly soluble in gasoline, better in water, readily soluble in alcohol. Boiling with 0.1 N hydrochloric acid and 0.1 N caustic alkali leads to saponification of the acetyl radical and to formation of 2-hydroxymethylbenzimidazole. Heating with boiling glacial acetic acid does not modify the compound, whereas heating with acetic anhydride for 20-25 minutes leads to formation of 1-acetyl-2-acetoxymethylbenzimidazole, which after crystallization from a mixture of gasoline and benzene melts at 97-98°.

Silver salt. 1.5 g of 2-acetoxymethylbenzimidazole is dissolved in 15 ml alcohol; a solution of 1.5 g silver nitrate in 5 ml water, to which 5 ml concentrated aqueous ammonia has previously been added, is run in. The resultant precipitate is filtered and washed with alcohol and water. Yield 2.32 g (theoretical) of fine white crystals.

0.3311 g substance: 0.1199 g Ag. 0.4233 g substance: 0.1528 g Ag. Found %: Ag 36.21, 36.10.
$C_{10}H_9O_2N_2Ag$. Calculated %: Ag 36.32.

Iodoamine. 0.5 g 2-acetoxymethylbenzimidazole is dissolved in 150 ml hot water; to the ice-cooled solution is added 4 ml 25% NaOH and (dropwise with constant stirring) 52.1 ml (the theoretical amount) of 0.1 N solution of iodine in potassium iodide. Yield 0.82 g white amorphous powder with m.p. 164° (with decomposition). The percentage content of iodine in the obtained product is determined iodometrically. A weighed amount of about 0.5 g 1-iodo-2-acetoxymethylbenzimidazole is introduced into a 250 ml measuring flask; 60 ml 10% KI solution and 25 ml 2 N hydrochloric acid are added. The contents are thoroughly shaken and gently heated to dissolve the precipitated black flocs. The transparent solution is made up to the mark with water. Titration is performed on 50 ml amounts of the solution.

0.4479 g substance: titration of 50 ml solution took on the average 5.56 ml 0.1 N $Na_2S_2O_3$.
Found %: I 39.38. $C_{10}H_9O_2N_2I$. Calculated %: I 40.15.

b) 1-Acetyl-2-acetoxymethylbenzimidazole. To 5 g 2 hydroxymethylbenzimidazole is added 5.g anhydrous sodium acetate in 20 ml acetic anhydride. The mixture is heated on a boiling water bath for 20 minutes. The liquid reagents are removed by evaporation and the residual crystalline mass is treated with a small quantity of ligroin. Yield 6.62 g (84%) of white prisms with m.p. 96 98°. After crystallization from a mixture of gasoline and benzene, the m.p. was 98-99.5°.

0.2111g substance: 22.6 ml N_2(21°, 760 mm). 0.1523 g substance: 16.4 ml N_2 (21°, 760 mm). 0.0359 g substance: 15.23 ml 0.02 N NaOH. Found %: N 12.43, 12.50; acetyl groups 36.53. $C_{12}H_{12}O_3N_2$.
Calculated %: N 12.06; acetyl groups 37.07.

The substance is sparingly soluble in water, alcohol, and gasoline, slightly better in benzene. Boiling with water for 10 minutes results in a quantitative yield of 2-acetoxymethylbenzimidazole with m.p. 163-164°. On prolonged storage the product decomposes.

c) 1-Methyl-2-acetoxy methylbenzimidazole. A mixture of 3.2 g 1-methyl-2-hydroxymethylbenzimidazole, 2.5 ml (30% excess) acetic anhydride, and 7 ml glacial acetic acid is heated for an hour on a boiling water bath. The liquid is evaporated to dryness; the resultant yellow oil is worked up with absolute ether to give 2.54 g (63%) of a white substance which after two crystallizations from a 3:1 mixture of gasoline and benzene gives white needles with m.p. 76-78°.

0.1190 g substance: 14.2 ml N_2 (20°, 757 mm). 0.1039 g substance: 12.2 ml N_2 (20°, 764 mm).
Found %: N 13.84; 13.75. $C_{11}H_{12}O_2N_2$. Calculated %: N 13.72.

d) Acetylation of the methoiodide of 1-methyl-2-hydroxymethylbenzimidazole. 6 g (0.02 mole) methoiodide of 1-methyl-2-hydroxymethylbenzimidazole, 2.6 ml (30% excess) acetic anhydride, and 10 ml glacial acetic acid are heated on a boiling water bath for 1.5 hour. The dark red crystals(3.8 g) are filtered off; to the filtrate is added absolute ether; a yellow oil is precipitated and is converted into a white solid after two treatments with absolute ether and chloroform; after two crystallizations from the minimum volume of absolute alcohol, it gives 0.4 g product with m.p. 256-258° (with decomposition). The 3.8 g of filtered dark crystals is treated with 60-70 ml dry chloroform; a large proportion goes into solution, leaving 0.28 g of the above-described by-product. The chloroform solution is washed with a small quantity of an aqueous solution of thiosulfate in order to remove iodine; the water is separated; the chloroform layer is dried with calcium chloride and the solvent is driven off, leaving 1.65 g of a substance which, after three crystallizations from absolute alcohol gave about 0.5 g pinkish leaflets with constant m.p. of 164-165°.

0.1697 g substance: 0.1141 g AgI. 0.1659 g substance: 0.1120 g AgI. Found %: I 36.35, 36.50.
$C_{12}H_{15}O_2N_2I$. Calculated %: I 36.67.

Analysis of the high-melting by-product with m.p. 256-258° gave the following results.

0.1289 g substance: 0.1029 g AgI. 0.1211 g substance: 0.0966 g AgI. Found %: I 43.15, 43.12.

3. Benzoylation of 2-hydroxymethylbenzimidazole and of the products of its methylation.

a) Benzoylation of 2-hydroxymethylbenzimidazole. Benzoylation is effected in a chlorobenzene medium by the action of benzoyl chloride on the hydrochloride of 2-hydroxymethylbenzimidazole. 5.4 g (0.03 mole) thoroughly ly dried and pulverized 2-hydroxymethylbenzimidazole hydrochloride is suspended in 100 ml boiling chlorobenzene and dropwise addition is made of 4.1 ml (5.0g, 20% excess) benzoyl chloride in 15 ml chlorobenzene. After boiling for 6 hours, the mass is cooled and the precipitate filtered off. Yield 4.88 g (57.7%) of 2-benzoylhydroxymethylbenzimidazole; , it is washed with pure chlorobenzene. The filtrate and wash liquor are combined and the chlorobenzene is distilled off to leave a small amount of oil which partially solidified after 24 hours. Ether extraction removed 2.0 g unsolidified oil, leaving 1.46 g (14.5% of theoretical) of 1-benzoyl-2-benzoylhydroxymethylbenzimidazole.

2-Benzoylhydroxymethylbenzimidazole. White, lustrous hexagonal leaflets with m.p. 146-147°. Crystallizes from aqueous alcohol or from a mixture of benzene and gasoline. Soluble in alcohol, benzene and acetone; insoluble in water and gasoline.

0.1272 g substance: 0.3342 g CO_2; 0.0557 g H_2O. 0.1356g substance: 0.3563 g CO_2; 0.0584 g H_2O. 0.2257 g substance: 32.46 ml 0.1 N. NaOH. 0.2409 g substance: 31.23 ml 0.1 N NaOH. 0.0258 g substance: 5.09 ml 0.02 N NaOH. 0.0237 g substance: 4.73 ml 0.02 N NaOH. Found %: C 71.65, 71.67 H 4.90, 4.82; N 10.97, 10.99 (Kjeldahl); benzoyl groups 41.47, 41.95. $C_{15}H_{12}O_2N_2$. Calculated %: C 71.43; H 4.80; N 11.11; benzoyl groups 41.66.

The base is not saponified by dilute inorganic acids; boiling with 4 N hydrochloric acid leads to the hydrochloride with m.p. 233-235°; crystallizes from water or alcohol.

0.0682 g substance: 0.0337 g AgCl. 0.1975 g substance: 0.0968 g AgCl. Found % Cl 12.22, 12.13. $C_{15}H_{13}O_2N_2Cl$. Calculated %: Cl 12.28.

Boiling with 4 N sulfuric acid gives the acid sulfate in the form of white, lustrous crystals with m.p. 207-210°; purified by crystallization from dilute sulfuric acid.

0.5636 g substance: 0.3794 g $BaSO_4$. 0.4431 g substance: 0.2968 g $BaSO_4$. Found %: S 9.25, 9.20. $C_{15}H_{14}O_6N_2S$. Calculated %: S 9.15.

The silver salt was prepared in conditions similar to those for the salt of 2-acetoxymethylbenzimidazole. White crystals; yield 88.8% of the theoretical.

0.2964 g substance: 0.0888 g Ag. 0.3010 g substance: 0.0902 g Ag. Found %: 29.96, 29.97. $C_{15}H_{11}O_2N_2Ag$. Calculated %: Ag 30.04.

1-Benzoyl-2-benzoylhydroxymethylbenzimidazole. White, irregularly shaped crystals with m.p. 89-91°, soluble in alcohol, acetone and benzene; insoluble in water gasoline, ether and dilute hydrochloric and sulfuric acids; it decomposes when boiled with inorganic acids with formation of salts of 2-benzoylhydroxymethylbenzimidazole.

0.1522 g substance: 21.17 ml 0.1 N NaOH. 0.5148 g substance: 20.97 ml 0.1 N NaOH. 0.0216 g substance: 6.30 ml 0.02 N NaOH. 0.0230 g substance: 6.68 ml 0.02N NaOH. Found %: N 8.02, 8.03 (Kjeldahl); benzoyl groups 61.31, 61.05. $C_{21}H_{16}O_3N_2$. Calculated %: N 8.14; benzoyl groups 61.05.

The dark yellow oil formed during benzoylation is soluble in acetone, methyl and ethyl alcohols, benzene, toluene, pyridine, ether and chloroform; less soluble in gasoline, insoluble in water. Treatment in the cold with 4 N hydrochloric acid converts it into the hydrochloride of 2-benzoylhydroxymethylbenzimidazole, and benzoyl chloride and benzoic acid are separated. A similar decomposition is observed on lengthy standing of the oil in the air or on heating at 80-100°. The nitrogen determination (Kjeldahl) gave the following result:

0.4352 g substance: 34.00 ml 0.1 N NaOH. 0.5844 g substance: 27.89 ml 0.1 N NaOH. Found %: N 5.31, 5.42.

b) Benzoylation of 1-methyl-2-hydroxymethylbenzimidazole. To 3.24 g (0.02 mole) 1-methyl-2-hydroxymethylbenzimidazole suspended in 40 ml absolute benzene, 3.4 g (2.8 ml, 20% excess) benzoyl chloride in 10 ml absolute benzene is added. The mixture is heated at the boil for an hour, cooled, and filtered; the precipitate is repeatedly washed with pure absolute benzene to give 4.88-5.12 g (80.9-84.7%) of the hydrochloride of 1-methyl-2-benzoylhydroxymethylbenzimidazole. The product crystallizes from aqueous alcohol (1:4) or dilute hydrochloric acid in the form of long, snow-white needles with m.p. 195-197°. On drying it partly loses HCl.

0.0867 g substance: 0.0388 g AgCl. 0.1007 g substance: 0.0446 g AgCl. Found %: Cl 11.08, 10.96. $C_{16}H_{15}O_2N_2Cl$. Calculated %: Cl 11.71.

The base is obtained by treating the hydrochloride with ammonia. After crystallization from water or gasoline, the rhombic crystals melt at 144-146°. In the cold the compound is readily soluble in benzene, alcohol and acetone;

soluble when hot in water and gasoline.

0.0915 g substance: 8.5 ml N_2 (22°, 762 mm). 0.1062 g substance: 9.9 ml N_2 (24°, 762 mm). Found %: N 10.78, 10.74. $C_{16}H_{14}O_2N_2$. Calculated %: N 10.52.

SUMMARY

1. Acetylation and benzoylation of 2-hydroxymethylbenzimidazole proceeds in the first instance at the hydroxyl group of the compound ; subsequently disubsituted derivatives are formed in which the second radical of the organic acid is linked to one of the nitrogen atoms of the heterocycle. The nitrogen-methylated derivative – 1-methyl-2-hydroxymethylbenzimidazole – is only able to yield monoacyl derivatives in which the acyl radical enters at the hydroxyl group.

2. The methoiodide of 1-methyl-2-hydroxymethylbenzimidazole is capable of acetylation at the hydroxy group, but benzoylation cannot be effected.

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SYNTHESES WITH THE AID OF ACRYLONITRILE

XX. CYANOETHYLATION OF ESTERS OF α-AMINO ACIDS

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The cyanoethylation of many types of organic compounds [1] has been studied, but that of amino acids has hardly been studied. Only in recent years have papers been published on the cyanoethylation of α-amino acids [2,3,4,5]. Considering that cyanoethylated derivatives of amino acids are of great interest, we turned our attention to their formation.

In the present communication we set forth the results of our experiments on the cynoethylation of esters of α-amino acids and their hydrochlorides. Depending on the conditions, the reaction products are N-mono- and N,N-dicyanoethylated esters

$$C_2H_5O_2C-CH_2-NH_2 \xrightarrow{CH_2=CH-CN} C_2H_5O_2C-CH_2-NH-CH_2-CH_2-CN \xrightarrow{CH_2=CH-CN} C_2H_5O_2C-CH_2-N(CH_2-CH_2-CN)_2.$$

By suitable choice of conditions we can obtain N-monocyanoethylated derivatives without appreciable contamination with N,N-dicyanoethylated compounds.

The materials which we cyanoethylated were the methyl and ethyl esters of glycine and their hydrochlorides, also he hydrochloride of the ethyl ester of phenylalanine. Cyanoethylation of the esters gave only N-monocyanoethylated derivativesin yields of 55 to 70% Cyanoethylation of glycine ester hydrochlorides by heating for an hour at 70-75° with three times the amount of acrylonitrile gave N-monocyanoethylated derivatives in yields of 51 to 68%. After 10 hours' heating, N,N-dicyanoethylated esters of glycine were isolated in addition to the N-mono-derivatives. Cyanoethylation of phenylalanine ethyl ester hydrochloride gave, regardless of the duration of heating, only the N-monocyanoethylated derivative in 78% yield.

The most important side reaction appears to be the formation of cyclic anhydrides, since the process is conducted in presence of alkalies or bases. Moreover the yields of N-cyanoethylated derivatives in the case of the easily cyclized methyl esters of glycine were always lower than in experiments with ethyl esters of glycine and with the hydrochlorides of the ethyl esters of glycine and phenylalanine.

The action of acrylonitrile on N-monocyanoethylated derivatives both without a catalyst and in presence of catalysts (NaOH, triethylamine), but in an anhydrous medium, didnot lead to formation of dicyanoethylated derivatives. But heating of esters of N-monocyanoethylated glycine in water with excess of acrylonitrile for 10 hours at 70-75° leads to preparation of dicyanoethylated derivatives in a yield of about 36%.

Esters of cyanoethylated amino acids are colorless liquids (some of them could be made to crystallize); they distil in vacuum and decompose when distilled not in vacuum. They give a negative ninhydrin reaction.

When treated with an ethereal solution of hydrogen chloride, they form the corresponding hydrochlorides; with an alcoholic solution of ammonia they give the corresponding amides of N-cyanoethylated amino acids. The hydrochlorides of the esters and the amides of cyanoethylated amino acids are crystalline substances.

EXPERIMENTAL

1. Methyl Ester of N Monocyanoethylaminoacetic Acid. $CH_3O_2C-CH_2-NH-CH_2-CH_2-CN$

a) to 5 g (0.056 mole) freshly distilled methyl glycinate in absolute ether is added 6 g (0.112 mole) acrylonitrile. The mixture is left for 3 days and then boiled under a reflux condenser for 5 hours. A considerable amount of diketopiperazine is precipitated during this treatment. After separating the precipitate and distilling off the ether, the reaction product is vacuum-distilled: b.p. 142-143° at 12 mm. Yield 4.4 g, i.e. 55.2% Colorless liquid, soluble in water, ethanol and ether. n_D^{20} 1.4530; d_4^{20} 1.0983; MR_D 34.99; calculated 34.98.

7.608 mg substance: 14.277 mg CO_2; 4.912 mg H_2O. 7.523 mg substance: 14.145 mg CO_2; 4.860 mg sub- H_2O. 77.1 mg substance: 10.91 ml 0.1 N H_2SO_4. 75.3 mg substance: 10.6 ml 0.1 N H_2SO_4. Found %: C C 51,21, 51 31; H 7.22, 7.22; N 19.80, 19.71. $C_6H_{10}O_2N_2$. Calculated %: C 50.69, H 7.09, N 19.77.

The hydrochloride was prepared by adding an ethereal solution of HCl. Crystals (from ethanol), m.p. 137°; readily soluble in water and boiling ethanol. Found %: Cl 19.53, 19.79. $C_6H_{11}O_2N_2Cl$. Calculated %: Cl 19.85.

b) Into a three-necked, round-bottomed flask, fitted with mechanical stirrer, a reflux condenser and dropping funnel was introduced 10 g (0.08 mole) methyl glycinate hydrochloride. Addition was made of 5 ml water, 12.6 g (0.24 mole) acrylonitrile and (with stirring for 15 minutes at 50°) 4.4 g (0.08 mole) KOH dissolved in 15 ml water. The mixture was heated for an hour at 70-75°. The reaction product was separated from the aqueous layer and the latter was extracted 3-4 times with ether. The ethereal extracts, together with the upper layer, were dried with sodium sulfate. After driving off the ether and the excess of acrylonitrile, the methyl ester of N-monocyanoethylglycine was distilled in vacuum. B.p. 142-143° at 12 mm. Yield 5.8 g (51.3%).

2. Methyl Ester of N, N-Dicyanoethylglycine. $CH_3O_2C{-}CH_2{-}N(CH_2{-}CH_2{-}CN)_2$

The reaction was conducted as in experiment 1 b. The amounts of reactants were the same. The mixture was heated for 10 hours at 70-75°. The methyl ester of N-monocyanoethylglycine boils at 142-143° at 12 mm. Yield 2 g (17.8%). The boiling point of the methyl ester of N, N-dicyanoethylglycine is 218-219° at 12 mm. Yield 3.4 g (21.9%). Colorless oil, crystallizing when cooled with ice. M.p. 59.5-60° (from water); readily soluble in ethanol, ether and hot water; less easily in cold water.

7.355 mg substance: 14.876 mg CO_2; 4.413 mg H_2O. 6.575 mg substance: 13.318 mg CO_2; 3.970 mg H_2O. 73.9 mg substance: 11.33 ml 0.1 N H_2SO_4. 71.1 mg substance: 10.91 ml 0.1 N H_2SO_4. Found %: C 55.20, 55.28; H 6.71, 6.76; N 21.46, 21.47. $C_9H_{13}O_2N_3$. Calculated %: C 55.36; H 6.71; N 21.52.

The hydrochloride forms crystals with m.p. 121-121.5° (from ethanol); readily soluble in water and boiling ethanol. Found %: Cl 15.25, 15.17. $C_9H_{14}O_2N_3Cl$. Calculated %: Cl 15.30.

3. Ethyl Ester of N-Monocyanoethylglycine. $C_2H_5O_2C{-}CH_2{-}NH{-}CH_2{-}CH_2{-}CN$

a) The reaction was performed as in experiment 1a. To 5 g (0.048 mole) ethyl glycinate is added 5.1 g (0.096 mole) acrylonitrile. The boiling point of the ethyl ester of N-monocyanoethylglycine is 148-149° at 12 mm. Yield 5.3 g (70.5%). Colorless liquid, soluble in water, ethanol and ether. n_D^{20} 1.4498; d_4^{20} 1.0615; MR_D 39.52; Calculated: 39.60.

6.820 mg substance: 13.390 mg CO_2; 4.810 mg H_2O. 5.785 mg substance: 11.385 mg CO_2; 4.132 mg H_2O. 106.2 mg substance: 13.8 ml 0.1 N H_2SO_4. 109.9 mg substance: 14.25 ml 0.1 N H_2SO_4. Found %: C 53.58, 53.71; H 7.89, 7.99; N 18.19, 18.15. $C_7H_{12}O_2N_2$. Calculated %: C 53.82; H 7.74; N 17.93.

The hydrochloride forms crystals with m.p. 113° (from ethanol); readily soluble in water and boiling ethanol.

Found %: Cl 18.04, 18.35. $C_7H_{13}O_2N_2Cl$. Calculated %: Cl 18.40.

N-Monocyanoethylglycinamide was prepared by treating 3 g of ethyl ester of N-monocyanoethylglycine with 45 ml of methanol solution of ammonia saturated at 0°. The solution was kept for 24 hours after which the methanol and excess ammonia were removed by evaporation in vacuum. The solid residue was recrystallized. Platelets (from ethanol), m.p. 46-47°. Yield 1.9 g (79.2%). Soluble in water, ethanol and chloroform; insoluble in ether.

7.690 mg substance: 13.350 mg CO_2; 4.890 mg H_2O. 8.690 mg substance: 15.100 mg CO_2; 5.600 mg H_2O. 46.6 mg substance: 11.0 ml 0.1 N H_2SO_4. 51.6 mg substance: 12.16 ml 0.1 N H_2SO_4. Found %: C 47.37, 47.39; H 7.12, 7.21; N 33.05, 32,98. $C_5H_9ON_3$. Calculated %: C 47.23; H 7.13; N 33.05.

b) The reaction was performed as in experiment 1 b. To 10 g (0.07 mole) ethyl glycinate hydrochloride were added 5 ml water, 11.4 g (0.21 mole) acrylonitrile and 4 g (0.07 mole) KOH dissolved in 15 ml water, and the mixture was heated for an hour at 70-75°. The ethyl ester of N-monocyanoethylglycine boils at 148-149° at 12 mm. Yield 7.6 g (67.8%).

4. Ethyl Ester of N, N-Dicyanoethylglycine $C_2H_5O_2C-CH_2-N(CH_2-CH_2-CN)_2$

The reaction was performed as in experiment 1b.

The quantities of reactants were the same. The mixture was heated for 10 hours at 70-75°. The ethyl ester of N-monocyanoethylglycine boils at 148-149° at 12 mm. Yield 2.6 g (23.2%). The boiling point of the ethyl ester of N, N-dicyanoethylglycine is 221-222° at 12 mm. Yield 4.4 g (29.3%). Colorless oil which crystallizes when cooled with ice, but again changes into oil at room temperature. Readily soluble in ethanol, ether, and hot water; less readily soluble in cold water.

8.080 mg substance; 17.020 mg CO_2; 5.385 mg H_2O. 6.235 mg substance: 13.090 mg CO_2; 4.095 mg H_2O. 67.5 mg substance: 9.75 ml 0.1 N H_2SO_4. 55.7 mg substance: 8.05 ml 0.1 N H_2SO_4. Found %: C 57.48, 57.30; H 7.46, 7.35; N 20.22, 20.23. $C_{10}H_{15}O_2N_3$. Calculated %: C57.39; H 7.22; N 20.08.

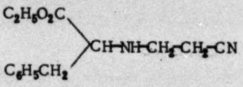
The hydrochloride forms crystals (from ethanol) with m.p. 121-121.5°; easily soluble in water and boiling ethanol.

Found %: Cl 14.23, 14.38. $C_{10}H_{16}O_2N_3Cl$. Calculated %: Cl 14.43.

N,N-Dicyanoethylglycinamide was prepared as in experiment 3a by treating 4 g ethyl N,N-dicyanoethylglycinate with 60 ml of methanol solution of ammonia. Platelets (from ethanol) with m.p. 95.5°. Yield 3 g (81.4%). Soluble in water and ethanol; insoluble in ether.

8.100 mg substance: 15.870 mg CO_2; 4.910 mg H_2O. 6.320 mg substance: 12.430 mg CO_2; 3.910 mg H_2O. 49.8 mg substance: 11.01 ml 0.1 N. H_2SO_4. 52.6 mg substance: 11.64 ml 0.1 N. H_2SO_4. Found %: C 53.47, 53.67; H 6.78, 6.92; N 30.94, 30.97. $C_8H_{12}ON_4$. Calculated %: C 53.31; H 6.71; N 31.09.

5. Ethyl Ester of N-Monocyanoethyl-β-phenylalanine



$$\begin{matrix} C_2H_5O_2C \diagdown \\ \quad CH{-}NH{-}CH_2{-}CH_2{-}CN \\ C_6H_5CH_2 \diagup \end{matrix}$$

The reaction was performed as in experiment 1 b. To 10 g (0.04 mole) phenylalanine ethyl ester hydrochloride was added 5 ml water, 6.8 g (0.12 mole) acrylonitrile and 2.4 g (0.04 mole) KOH dissolved in 15 ml water, and the mixture was heated for 5 hours at 70-75°. The boiling point of the ethyl ester of N-monocyanoethylphenylalanine is 191-192° at 8 mm. Yield 8.4 g (78.5%); Colorless liquid, soluble in ethanol and ether, insoluble in water.

n_D^{20} 1.5110; d_4^{20} 1.0763; MR_C Found 63.77; Calculated 63.22.

3.085 mg substance: 7.706 mg CO_2; 2.080 mg H_2O. 4.965 mg substance: 12.400 mg CO_2; 3.294 mg H_2O. 134.1 mg substance: 11.0 ml 0.1 N. H_2SO_4. 111.6 mg substance: 9.03 ml 0.1 N. H_2SO_4. Found %: C68.17, 68.16; H 7.54, 7.42; N 11.48, 11.33. $C_{14}H_{18}O_2N_2$. Calculated %: C 68.27; H7.36; N 11.37.

The hydrochloride forms platelets (from ethanol) with m.p. 166°; readily soluble in water and boiling ethanol.

Found %: Cl 12. 56, 12.44. $C_{14}H_{19}O_2N_2Cl$. Calculated %: Cl 12.54.

The amide of N-monocyanoethylphenylalanine was prepared as in experiment 3a by standing 2 g ethyl ester of N-monocyanoethylphenylalanine with 50 ml methanol solution of ammonia for 5 days. Lustrous platelets (from ethanol) with m.p. 108.5°. Yield 1.4 g (82.3%). Soluble in water and ethanol.

8.125 mg substance: 19.618 mg CO_2; 5.000 mg H_2O. 5.597 mg substance: 13.518 mg CO_2; 3.515 mg H_2O. 68.3 mg substance: 9.4 ml 0.1 N H_2SO_4 64.2 mg substance: 8.8 ml 0.1 N H_2SO_4. Found %: C C 65.89, 65.91; H 6.89, 7.03; N 19.27, 19.19. $C_{12}H_{15}ON_3$. Calculated %: C 66.33, H 6.96; N 19.34.

SUMMARY

The reaction of acrylonitrile with esters of amino acids and their hydrochlorides was studied.

The following were prepared and characterized for the first time: the methyl and ethyl esters of N-mono- and N,N-dicyanoethyl-glycine and the ethyl ester of N-monocyanoethyl-phenylalanine, also their hydrochlorides.

The action of ammonia on the esters of N-cyanoethyl-amino acids was studied. For the first time prepared and characterized were the amides of N-mono- and N,N-dicyanoethyl-phenylalanine.

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THE REACTION OF ARYL SULFAMIDES WITH AMINES. II.

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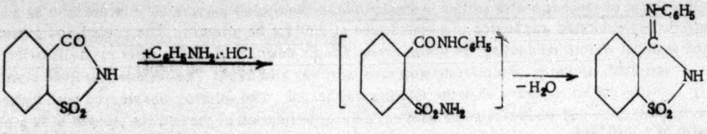
In the preceding communication [1] it was pointed out that amines which form amides of aromatic sulfonic acids are displaced in certain conditions by primary aromatic amines. If the primary amine is replaced by a tertiary one, for example dimethylaniline, then the latter in these cases splits off one methyl group, and the formed monomethylaniline displaces the radical of the primary amine from the sulfamide group.

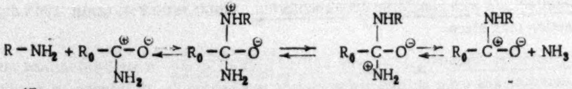
The process of displacement may also be regarded as an acylation of the primary or secondary amine by sulfamides.

In connection with our studies of aminolysis of sulfamides it seemed of interest to apply the catalytic action of hydrogen chloride [1] to the rupture of the isothiazole ring of saccharin not only at the C–N bond but also at the S–N sulfamide linkage. The ammonia released in this reaction, by combining with the hydrogen chloride, should form ammonium chloride which in the given conditions should be removed from the sphere of reaction as a solid phase.

On heating saccharin with aniline hydrochloride in a sealed tube at 200° for 15 minutes, however, the main reaction proved to be dehydration, leading to formation of phenylpseudosaccharin

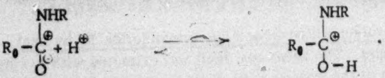


In regard to the mechanism of the process in question, attention may be directed to the views of B. A. Porai-Koshits [2,3] on the acylation of amines which, in our opinion, can be extended to a series of other reactions and, in particular, to the acylation of amines by carboxylic acid amides:



$$\underset{(I)}{R-NH_2} + \underset{(II)}{R_0-\overset{\oplus}{\underset{NH_2}{C}}-\overset{\ominus}{O}} \rightleftarrows \underset{(III)}{R_0-\overset{\overset{\oplus}{N}HR}{\underset{NH_2}{C}}-\overset{\ominus}{O}} \rightleftarrows \underset{(IV)}{R_0-\overset{NHR}{\underset{\overset{\oplus}{N}H_2}{C}}-O^{\ominus}} \rightleftarrows \underset{(V)}{R_0-\overset{NHR}{\overset{\oplus}{C}}-\overset{\ominus}{O}} + NH_3$$

According to this scheme, only the free amine enters into reaction; the intermediate product (III) is formed by entry of the unshared electron pair of nitrogen (I) into the electron-deficient system of the carbon atom of the carbonyl group of the amide which reacts in the polarized form (II). Stabilization of the intermediate product is effected as a result of separation of a molecule of the other amine, an important part in this process being played by the degree of basicity of the competing amines. The catalytic activity of hydrogen ions in this reaction must be associated with the considerable polarization of the double bond of the carbonyl group due to addition of a proton to the oxygen and to formation of a cation with an electron deficiency at the carbon atom:

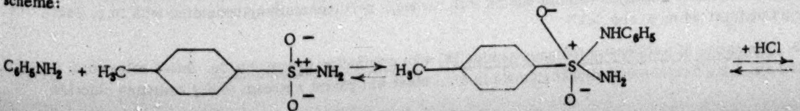


$$R_0-\overset{NHR}{\underset{O^{\ominus}}{C^{\oplus}}} + H^{\oplus} \longrightarrow R_0-\overset{NHR}{\underset{O-H}{C^{\oplus}}}$$

Smith and Adkins [4] have also drawn attention to the possibility of formation of an intermediate addition product.

To a certain extent, such a reaction mechanism ought to be applicable to the process of acylation of amines by sulfonic acid amides [5].

For example, the interaction of p-toluenesulfanilide with aniline might be represented by the following scheme:



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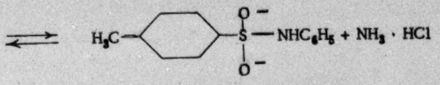
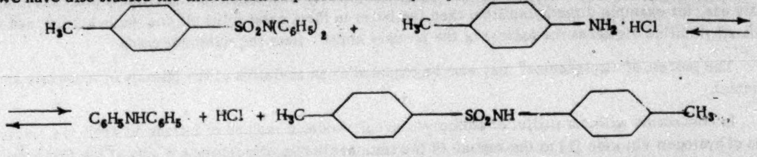


In that event, the center of addition of the amine is the electronophilic atom of sulfur and not the carbon atom in carbamides.

As was indicated previously [1], the phase equilibria factors exert a considerable influence on the course of the investigated exchange reaction. Supplementary date on this matter are presented in the experimental part.

We have also studied the interaction of p-toluenesulfodiphenylamide with p-toluidine hydrochloride:



where the release of hydrogen chloride in the gas phase facilitated the course of the reaction from left to right.

EXPERIMENTAL

1. Interaction of saccharin with aniline hydrochloride. A thoroughly pulverized mixture of 0.92 g saccharin and 0.6 g aniline hydrochloride was heated in a sealed tube at 200° for 25 minutes. The cooled and pulverized mass was extracted with hot water; on cooling, yellowish crystals came down, m.p. 222°; after crystallization from alcohol the m.p. was 225°; the m.p. of a mixture with saccharin was also 225°. The residue dissolved completely in dilute alkali. Aniline did not separate when the solution was heated. The solution was treated with hydrochloric acid until weakly alkaline and was decolorized with carbon. Acidification of the filtrate yielded 0.72 g phenylpseudosaccharin with m.p. 315° [6].

2. Interaction of N,N'-di-p-toluenesulfonylbenzidine [7] with benzidine dihydrochloride. Molar ratio 1.4:1; temp. 320-340°; duration 5 minutes. There was no exchange reaction.

3. Interaction of p-toluenesulfanilide with benzidine dihydrochloride. Molar ratio 2:1; temp. 190°; duration 35 minutes. No exchange reaction took place.

4. Interaction of N,N'-di-p-toluenesulfonylbenzidine with aniline hydrochloride. A well-pulverized mixture of 0.8 g di-p-toluenesulfonylbenzidine and 0.6 g aniline hydrochloride was heated for 15 minutes in a sealed tube at 225-230°. After the tube had been cooled and opened, it was crushed and pulverized together with the contents and extracted several times with 1:1 hydrochloric acid. Benzidine was precipitated from the hydrochloric acid extracts on treatment with alkali; no precipitate came down when the alkaline solution was acidified. The benzidine was converted into the sulfate which was titrated with NaOH solution in presence of phenolphthalein. Yield 0.29 g (96.6% of the theoretical).

The precipitate after extraction was dissolved in 16 ml 10% NaOH solution. After filtration and decolorization with charcoal, fractional precipitation was effected by acidification. Fractions melting at 101-103° were obtained, corresponding to p-toluenesulfamide. Yield 0.74 g (93% of the theoretical).

5. Transformation of mono-p-toluenesulfonylbenzidine hydrochloride [8] by heat. The hydrochloride (0.5 g) was heated at 250° for 15 minutes. The pulverized melt was extracted with 1:1 hydrochloric acid while heating on the water bath. Treatment of the extracts with alkali brought down benzidine. The amount of the latter was determined as above. Yield 0.087 g (63% of the theoretical).

The alkaline filtrate after precipitation of benzidine base was treated with hydrochloric acid until weakly alkaline, decolorized with carbon and finally acidified with acetic acid. A white precipitate of the unchanged mono-derivative came down, m.p. 164°. A mixed test also gave m.p. 164°.

The residue of the melt was pulverized and reprecipitated with hydrochloric acid from a large volume of dilute sodium hydroxide solution (decolorization with carbon). p-Toluenesulfonylbenzidine with m.p. 241° was precipitated; mixed m.p. also 241°.

6. Interaction of p-toluenesulfodiphenylamide [9] with p-toluidine hydrochloride. Into a solution of 0.56 g p-toluidine and 1.3 g p-toluenesulfodiphenylamide in 5 ml ether was passed a stream of dry hydrogen chloride

until saturated. After driving off the ether, the mixture was heated at 185° for 30 minutes. The mass was washed with dilute hydrochloric acid and with hot water. From the aqueous extracts were precipitated colorless platelets of diphenylamine (m.p. 54°; mixed melting point also 54°). The alkaline extracts were gradually acidified with with 1 N hydrochloric acid and left overnight; p-toluenesulfo-p-toluidide came down and after crystallization from alcohol melted at 118° [10].

SUMMARY

1. The main product of reaction of saccharin with aniline hydrochloride is phenylpseudosaccharin.

2. New cases of interaction between arylsulfamides and hydrochlorides of amines were investigated.

3. Suggestions about the mechanism of the investigation reaction were advanced.

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* See Consultants Bureau Translation, p. 2101.

THE STRUCTURE OF THE NEW FUROCOUMARIN PRANGENINE

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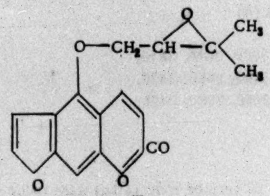
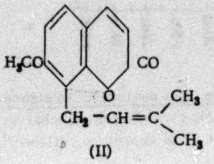
In 1948 [1] we investigated the secretion of the resinous runner roots of Prangos pabularia L.("ayu-chach"), a plant widely distributed in the mountain regions and foothills of the Kirghiz USSR). Examination of the resin showed that Prangos pabularia is a new source of coumarin derivatives. As we know, a large number of natural coumarins have been isolated from plants of the Umbelliferae family: Peucedanum officinale, Imperatoria ostruthium, Angelica Archangelica. Among the crystalline products isolated from the resin of Prangos pabularia, we found the furocoumarin hydroxypeucedanin (I) and osthole (II)

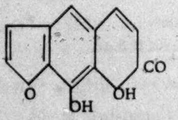


(I)

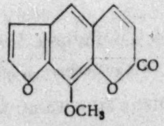


(II)

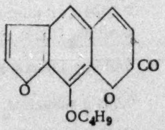
Apart from the substances mentioned, we also isolated from the ligroin extract a compound which after numerous crystallizations melted at 97°. The elementary analysis and the molecular weight determination permitted us to assign the formula $C_{15}H_{14}O_4$ to this compound. It had a neutral reaction and exhibited lactone-like properties. It was not precipitated from alkaline solution; on acidification of the alkaline solution (or on passing CO_2) it was separated unchanged. Dissolution in alkali in the absence of phenolic hydroxyls ought to be due to the presence of a lactone ring. In order to clarify the structure of this compound, we subjected it to hydrolysis with strong hydrochloric acid. A crystalline product was obtained; m.p. 245°, readily soluble in alkali. The elementary analysis, the molecular weight determination and the melting point permitted us to assign to it the formula $C_{11}H_{16}O_4$ and to identify it as xanthotoxol (III):



(III)



(IV)



(V)

In order to confirm the structure of the compound with m.p. 245°, we subjected it to methylation. This reaction gave a compound with m.p. 146°, corresponding to the product of methylation of xanthoxtoxol — xanthotoxin (IV). Consequently, the foregoing data confirm that the substance with m.p. 97°, which we isolated from the secretion of the roots of Prangos pabularia, is a derivative of xanthotoxol and is, accordingly, the new furocoumarin (V).

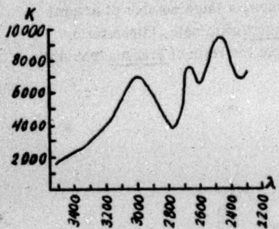
One unclarified feature of the new furocoumarin, which we have named prangenine, was the structure of the C_4H_9 radical of the side chain.

Assignment of the structure of a furocoumarin to prangenine is supported by its absorption spectrum. The spectrum was determined in ethyl alcohol (0.0226 mole/liter). A hydrogen lamp was chosen as the source of the continuous irradiation spectrum. The spectrum was plotted with the help of a Q-12 quartz spectrograph.

We see from the absorption curve that the absorption bands of prangenine are in the long-wave region of 3500-2200 A. The maxima of the absorption bands are λ = 3000, 2670, 2470 A (see diagram).

The absorption spectrum is very similar to the spectra of the furocoumarins xanthotoxol and hydroxypeucedanin.

The spectrum provides additional evidence of the furocoumarinic structure of prangenine:



Maxima of absorption bands (A)

Prangenine	3000, 2670, 2470.
Xanthotoxol	3055, 2650, 2470.
Hydroxypeucedanin . . .	3066, 2660, 2495.

EXPERIMENTAL

Isolation from the resin of substance with m.p. 97°. The air-dry pulverized roots (4 kg) were twice soaked with 95% alcohol; each time the alcohol was poured off after standing for 2 weeks. The total volume of the alcoholic extract was 40 l. The alcohol was driven off in vacuum, leaving a residue of 400 g (10%) of dark-brown, viscous mass.

The dark-brown mass was exhaustively extracted with ether while shaking. The ether was added in small portions of 200-300 ml each. The shaking operation with each fresh portion of ether was repeated until the ether did not extract anything more. All the ethereal extracts were combined and totalled 1½ l including 280 g resin (7% of the weight of roots). 700 ml ether was distilled off from the extract and the concentrated ethereal solution was left at rest for several days. After a few days crystals of hydroxypeucedanin with m.p. 142° came down. The ether was removed from the residual solution after saparation of these crystals and the residue was treated 5 times with hot ligroin, adding 150 ml solvent each time. A total of 750 ml ligroin extract was obtained, containing 30.8 g resin. Prolonged standing of the ligroin solution followed by evaporation led to separation of a mixture of compounds. This mixture was recrystallized several times. A compound with m.p. 96.5-97°. Recrystallization from alcohol gave white crystals with m.p. 97°.

0.0944 g substance: 0.2423 g CO_2; 0.0446 g H_2O. 0.0952 g substance: 0.2452 g CO_2; 0.0458 g H_2O. Found %: C 70.00, 70.24; H 5.28, 5.38. $C_{15}H_{14}O_4$. Calculated %: C 69.76; H 5.46.

0.0136 g substance; 0.2474 g camphor: Δt 9° (Rast). Found: M 244. $C_{15}H_{14}O_4$. Calculated: M 258.

0.584 g substance: 0.0123 g KOH. Found: M 265. $C_{15}H_{14}O_4$. Calculated: M 258.

Hydrolysis of compound with m.p. 97° (preparation of xanthotoxol). To 1 g of the substance, dissolved in ethyl alcohol at 50°, was added 1 ml conc. hydrochloric acid; the reaction mixture was then left for 24 hours. The next day acicular crystals were separated from the solution and melted at 245° (decomp.) after crystallization from alcohol. The crystals dissolved readily in alkali to a yellowish-green solution.

0.0630 g substance: 0.1500 g CO_2; 0.0180 g H_2O. Found %: C 64.98; H 3.19. $C_{11}H_6O_4$. Calculated %: C 65.34; H 2.97. 0.712 g substance: 0.1982 g KOH. Found: M 202. $C_{11}H_6O_4$. Calculated: M 202.

Methylation of substance with m.p. 245° (preparation of xanthotoxin). 0.0712 g substance, dissolved in methyl alcohol, was treated with 0.1 N KOH until the solution was weakly alkaline. After addition of 0.04 g CH_3 the mixture was refluxed for an hour. After removal of the alcohol, the mixture was diluted with water and extracted with ether The ethereal solution was washed with 1% alkali solution and with water before drying. The ether was evaporated and white crystals came down which melted at 146° (from ether).

SUMMARY

In the secretion of the resinous runner roots of Prangos pabularia was found, apart from hydroxypeucedanin an osthole (previously discovered by us), a new furocoumarin, $C_{15}H_{14}O_4$, named prangenine. It is a derivative of xanthotoxol.

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CHROMIUM DIOXIDE--PREPARATION, PROPERTIES, AND ENTHALPY OF FORMATION

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Chromium oxides with compositions intermediate between Cr_2O_3 and CrO_3 have been the subject of many researches. Preparations with such compositions are obtained either by decomposing chromyl chloride, CrO_2Cl_2 [1,2,3,4], by decomposing chromic anhydride [5,6,7,8,9,10], or by oxidizing hydrated chrome oxide using oxygen [11,12,13]. Certain authors believe that these preparations have variable composition phases, $CrO_{2.6}$–$CrO_{2.2}$ and $CrO_{1.9}$–$CrO_{1.7}$ [14], others that a definite compound, CrO_2, exists.

The magnetic properties of these oxides were also studied; it was found that some of them were ferromagnetic, but even in this regard data of various investigators are contradictory [4,5,15]. Results of roentgenographic investigation likewise either did not lead to definite conclusions on the nature of the intermediate chromium oxides or showed that the authors were dealing with a mixture of several crystalline phases [6].

Synthesis of Chromium Dioxide.

Assuming that the different results of the several investigators could be explained by the fact that the authors were dealing with samples obtained under conditions where they were not at thermodynamic equilibrium with the products of decomposition, we decided to study the process of decomposing chromium anhydride under the condition of a high oxygen pressure.

In this it was found that decomposition of chromium anhydride at a temperature of 420–450° C and at an oxygen pressure of 200–300 atmospheres, produced a black colored substance, the composition of which was the same in all experiments, and corresponded to the formula $CrO_{1.98}$, i.e., was very close to the formula of chromium dioxide.* Analysis was performed both by determining the amount of weight loss on decomposition by calcination to 800°, and also by decomposition in a vacuum with subsequent measurement of the oxygen volume separated thereby. Comparison of results obtained by both methods shows that the compounds prepared under the stated conditions were anhydrous.

Roentgenographic Investigation

A sample, held for a long time at 450° with an oxygen pressure of 280 atmospheres, gave a powder picture, which, as is apparent from Figure 1 ($CrO_{1.98}$), seems sufficiently clear for its indication. In Table 1 are given the interplanar spacing values found by us and the results of identification according to the Bistrom curves. This identification shows that $CrO_{1.98}$ forms a lattice with tetragonal syngony. The elementary call parameters were: $a = 4.394 \pm 0.015$, $c = 5.77 \pm 0.02$, $c/a = 1.31$. The density of this preparation measured pycnometrically in cyclohexane was found to be 4.90 g/cm^3 (25° C). If we assume that the elementary cell contains 4 CrO_2 "molecules", then the roentgenographic density appears equal to 4.97 g/cm^3, which is in good agreement with the value found pycnometrically.

Magnetic Properties

Measurement of magnetic susceptibility, performed by the "cylinder method", showed that at room temperature the magnetic susceptibility value depended on field strength (Figure 2), i.e., chromium dioxide is ferromagnetic.

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* It is probable that we have a case of structure defects here. However, the closeness of this formula to the CrO_2 formula does not deprive us of the possibility of calling this compound the dioxide and of using the formula CrO_2 in qualitative discussion, similar to the fact that they write "FeO" although a stable phase of this composition, as is known, does not exist.

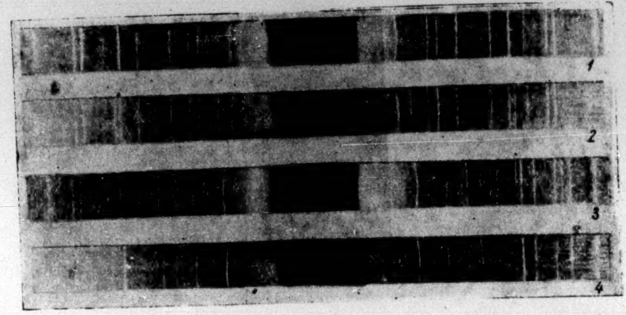

Fig. 1. Powder pictures of chromium oxides of varying composition: 1) $CrO_{1.50}$, 2) $CrO_{1.62}$, 3) $CrO_{1.95}$, 4) $CrO_{1.98}$. The Roentgenograms were taken with a camera having a diameter of 57.3 mm, on chromium radiation with a vanadium filter. The sample diameter was 1 mm. Potential was 25 kilovolts, current strength 20 milliamperes, exposure 3 hours.

TABLE 1

Results of Roentgenographic Identification

Line number	Interplanar spacing, A	Intensity (visual)	Index
1	3.08	Strong	110
2	3.41	Average	102
3	2.19	Weak	200
4	2.11	Average	112
5	1.97	Weak	210
6	1.62	Strong	113
7	1.55	Strong	220
8	1.44	Average	203
9	1.390	Strong	310
10	1.311	Strong	114

The Curie temperature was found to equal 115° C, which is close to the value given by Zhukov [3] for one of the products from decomposing chromium anhydride (having the composition $CrO_{2.2}$). It should be noted that the particular magnetic property of chromium dioxide (ferromagnetism) in the series of dioxides of elements of the 1st inserted decade corresponds to a lattice structure peculiarity in this very series. Titanium, vanadium, and manganese dioxide (not ferromagnetic) have an elementary cell with similar values for parameter a (TiO_2 4.58, VO_2 4.54, CrO_2 4.394, MnO_2 4.398), but the value of parameter c for CrO_2 is approximately twice as large as for the dioxides of its neighboring elements [16] (TiO_2 2.95, VO_2 −2.88, CrO_2 −5.77, MnO_2 −2.867).

Bete and Sleiter [17] showed that the condition for appearance of ferromagnetism was the presence of particles with incomplete electronic levels having large values of the second quantum number, and a large value for the ratio of the distances between centers of the particles and their radii.

The first condition is satisfied, evidently, for all the dioxides; as regards the ratio just mentioned, it has the largest value for CrO_2:

	TiO_2	VO_2	CrO_2	MnO_2	MoO_2	WO_2
Ratio of distance between ion centers to ion radius ..	2.30	2.36	3.92	2.75	2.05	2.03

Results of measuring magnetic susceptibility at temperatures above the Curie point are given in Table 2, where they are compared with values calculated from assuming that CrO_2 was actually a dioxide, or from assuming that we were dealing here with chromates of trivalent chromium ($Cr_2O_3 \cdot CrO_3$).

The data of Table 2 show that the experimental magnetic susceptibility values for $CrO_{1.98}$ are closer to values calculated based on assuming the presence of tetravalent chromium ions in the lattice of this compound, i.e., we may consider that $CrO_{1.98}$ actually is a dioxide, and not a mixed oxide.

TABLE 2

Temperature, °C	Magnetic susceptibility per mole		
	Value		
	Experimental	Calculated for $Cr^{IV}O_2$	Calculated for $\frac{1}{3}Cr_2O_3 \cdot CrO_3$
225	8040	9100	11400
264	5800	6700	8400
320	4100	4900	6200

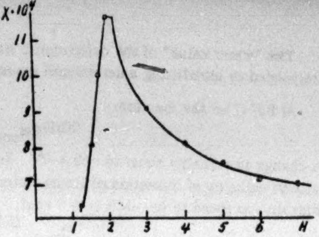

Fig. 2. Dependence of magnetic susceptibility, χ, of the $CrO_{1.98}$ preparation on field strength, H, (in arbitrary units) at room temperature.

It is pertinent to note that the magnetic susceptibility of molybdenum and tungsten dioxide, in contrast to the susceptibility of chromium dioxide, has a much lower theoretical value; this indicates the presence of bonds between the metallic ions. Probably, this difference may be set in relation to the larger enthalpy of sublimation value for molybdenum and tungsten (155 kcal for Mo and 210 kcal for W) as compared with the enthalpy of sublimation of chromium (89 kcal [18].)

Thermal Decomposition under Conditions Close to Equilibrium

For preliminary exploration of the width of the region of homogeneity for chromium dioxide, a series of experiments was set up decomposing chromium anhydride at 450° C at various oxygen pressures(duration of heating amounted to 8 hours in all cases).

The composition of the preparations obtained depended on the oxygen pressure in the following manner:

O_2 pressure, atm.	280	100	95	90	75
Composition:	$CrO_{1.98}$	$CrO_{1.98}$	$CrO_{1.82}$	$CrO_{1.92}$	$CrO_{1.62}$

Roentgenograms of products having the gross compositions $CrO_{1.92}$ and $CrO_{1.62}$ showed the presence of a Cr_2O_2 phase and a $CrO_{1.98}$ phase; here the interplanar distance in these latter seemed independent of pressure (Figure 1). We may thus conclude that $CrO_{1.98}$ does not have a perceptible region of homogeneity. It is of interest also in this connection that chromium dioxide occupies a particular place in the series of dioxides of the elements of the 1st inserted decade. Figure 3 presents dioxide existence regions for elements which neighbor chromium.

Enthalpy of Formation of Chromium Dioxide

The reaction most suitable for use in a calorimeter is the reaction reducing chromium dioxide by hydrogen, occurring according to the equation:

$$2CrO_2 + H_2 \longrightarrow Cr_2O_3 + H_2O.$$

This process was conducted at a hydrogen pressure of 20 atmospheres and was initiated using a heated spiral of fine platinum wire, placed in the chromium dioxide powder. To measure the change in temperature a resistance thermometer was used as one of the legs of a Wheatstone bridge.

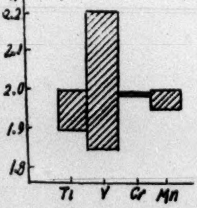

Fig. 3. Region of homogeneity for dioxides of elements in the 1st inserted decade.

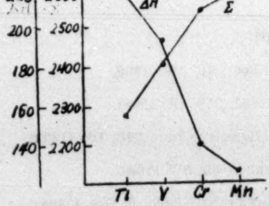

Fig. 4. Course of energy total for removing four electrons and the enthalpy of sublimation, Σ, for Ti, V, Cr, and Mn; and course of enthalpy of formation for corresponding dioxides, Δ H (kcal / mole).

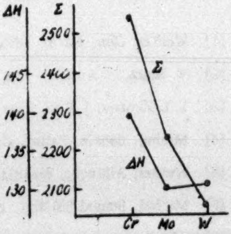

Fig. 5. Course of energy total for removing four electrons and enthalpy of sublimation, Σ, for Cr, Mo, and W, and course of enthalpy of formation Δ H (kcal/ mole) for corresponding dioxides.

The "water value" of the calorimetric bomb was determined by measuring the temperature rise which corresponded to introducing a determined quantity of energy into the bomb; it was measured potentiometrically.

At 25° C for the reaction:

$$2CrO_{1.98\,cryst} + 0.96H_{2\,gas} = CrO_{3\,cryst} + 0.96H_2O_{liquid}$$

a change in enthalpy equal to −59.8±0.5 kcal was found. From this, using an enthalpy of formation of −273 kcal, and an enthalpy of formation of liquid water equal to -68.37 kcal [18], the enthalpy of formation of chromium dioxide was found to be -139.4± 0.5 kcal.

$$Cr_{cryst} + 0.99O_{2\,gas} = CrO_{1.98\,cryst} + 139.4 \pm 0.5 \text{ kcal}.$$

It was shown by one of us [19] that the trend in heat of formation of binary compounds along a series of analogous compounds is often contrary to the trend in sum of corresponding valences, or in the sum of ionization potential and enthalpy of sublimation for the corresponding simple bodies to free atoms.

Figure 4 shows that this relation may be very clearly observed in the $TiO_2 - MnO_2$ series.

Matters are otherwise on transition from chromium to its analogs in the supplemental subgroup of group VI. Figure 5 shows that the converse relationship stated above does not exist in this case.

SUMMARY

1. Decomposition of chromium anhydride at temperatures of 420-450° C and oxygen pressures of 200-300 atmospheres leads to formation of anhydrous chromium dioxide.

2. Chromium dioxide has a tetragonal structure. The elementary cell dimensions are $\underline{c} = 5.77 \pm 0.02$ A, $\underline{a} = 4.394 \pm 0.15$ A, ($\underline{c}/\underline{a} = 1.31$), and contains 4 atoms of chromium and 8 oxygen atoms.

3. Chromium dioxide evidently does not have a very perceptible region of homogeneity.

4. Chromium dioxide is ferromagnetic; the Curie temperature was 115° C. The magnetic susceptibility above the Curie temperature was close to that calculated assuming that $CrO_{1.98}$ contains Cr^{4+} ions, i.e., that it was actually a dioxide, and not a mixture of oxides ($Cr_2O_3 \cdot CrO_3$).

5. The enthalpy of formation of chromium dioxide, found by calorimetric measurement of change in enthalpy during the reduction reaction with hydrogen to chromium oxide, was equal to -139.4 ± 0.5 kcal/mole:

$$Cr_{cryst} + 0.99O_{2\,gas} = CrO_{1.98\,cryst} + 139.4 \pm 0.5 \text{ kcal}$$

6. The trend in enthalpy of formation of TiO_2, VO_2, CrO_2, and MnO_2 is converse to the trend in the sum of enthalpy of sublimation for the corresponding metals and the energy for removing four electrons from their atoms. The trend in enthalpy of formation of chromium, molybdenum, and tungsten dioxides did not show this converse relation.

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REACTIONS IN FUSED NITRATES AND NITRITES OF METALS OF THE FIRST AND SECOND GROUPS OF THE D. I. MENDELEEV PERIODIC SYSTEM

VI. INVESTIGATION OF THE TERNARY SYSTEM RUBIDIUM NITRATE – POTASSIUM NITRATE – CADMIUM NITRATE

P. I. Protsenko and N. P. Popovskaya

It was previously reported [1] that potassium nitrate reacts with cadmium nitrate in a melt to form a complex compound, $Cd(NO_3)_2 \cdot 2KNO_3$, whose melting point is 199.5°. The clearly evident chemical affinity between the above noted components was observed not only in the binary, but also in a ternary system in presence of lithium nitrate as a third component. The present investigation has as a purpose exploration of the nature of reaction between rubidium and cadmium nitrates in the molten state, and also study of their effect on the previously described chemical compound.

The marked similarity, with regard to most physico-chemical properties, between potassium and rubidium nitrates forms the basis for predicting the nature of the relationship of rubidium nitrate to cadmium nitrate. This must be analogous to the relationship of potassium nitrate to cadmium nitrate, i.e., even in this case we should expect appearance of chemical reaction between the stated components. Here we should assume that the thermal stability of the proposed compound, $Cd(NO_3)_2 \cdot 2RbNO_3$, would be greater than the thermal stability of the compound $Cd(NO_3)_2 \cdot 2KNO_3$.

The experimental investigation performed, as will be shown below, confirmed our assumptions. Rubidium nitrate actually enters into chemical reaction with cadmium nitrate and forms the complex compound $Cd(NO_3)_2 \cdot 2RbNO_3$ with it. As regards the thermal stability of this compound, judging from its melting point, it seems somewhat less than that of the compound $Cd(NO_3)_2 \cdot 2KNO_3$.

EXPERIMENTAL

Binary systems. The equilibrium diagram for the binary system potassium nitrate – cadmium nitrate, which corresponds to one side of the triangular diagram of the above stated ternary system, has been previously described by one of us [1]. Investigation of the potassium nitrate – rubidium nitrate binary system, also corresponding to one side of the triangular diagram, showed that rubidium nitrate and potassium nitrate, in consequence of their marked similarity with regard to most physico-chemical constants, and in particular the very small difference in their atomic radii (rubidium 2.51 A, potassium 2.38 A), form a continuous series of solid solutions. The liquidus curve of this system is a smooth crystallization branch, bowed slightly toward the composition axis. The crystallization curve minimum is very weakly expressed. It corresponds to the composition:* 35 mole-% potassium nitrate and 65 mole % rubidium nitrate, with a m.p. of 296.5° (Fig. 1.).

The equilibrium diagram for the rubidium nitrate – cadmium nitrate system was studied for the first time by us. The liquidus curve for this system has three crystallization branches: cadmium nitrate, the chemical compound $Cd(NO_3)_2 \cdot 2RbNO_3$, and rubidium nitrate. The first eutectic point corresponds to the composition: 58.5% cadmium nitrate and 45.5% rubidium nitrate with a 167° m.p.; the second: 37% cadmium nitrate and 63% rubidium nitrate with a 172° m.p. The maximum on the chemical compound curve corresponds to a m.p. of 184° (Fig. 1).

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* Composition data are always given in mole percent throughout.

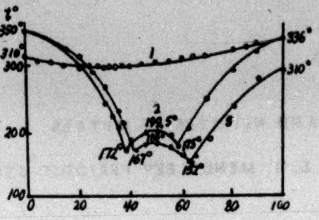

Fig. 1. Binary systems. 1—$RbNO_3$—KNO_3; 2—$Cd(NO_3)_2$—KNO_3; 3—$Cd(NO_3)_2$—$RbNO_3$

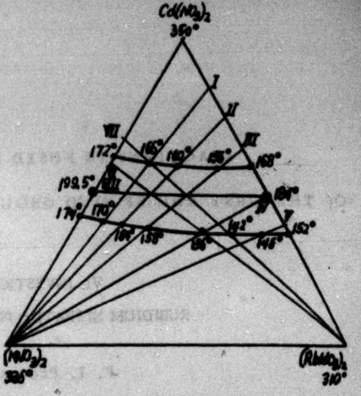

Fig. 2. Direction of sections in the ternary system.

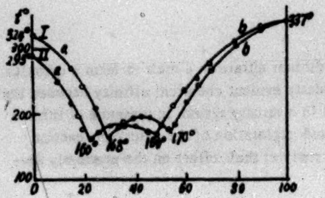

Fig. 3. Sections through ternary system:
I) 85% $Cd(NO_3)_2$ + 15% $(RbNO_3)_2$ → KNO_3;
II) 75% $Cd(NO_3)_2$ + 25% $(RbNO_3)_2$ → KNO_3;
a) $Cd(NO_3)_2$ branch; b) KNO_3 + $RbNO_3$ branch.

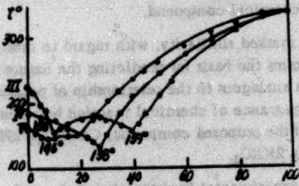

Fig. 4. Sections through ternary system:
III) 65% $Cd(NO_3)_2$ + 35% $(RbNO_3)_2$ → $(KNO_3)_2$;
IV) 50% $Cd(NO_3)_2$ + 50% $(RbNO_3)_2$ → $(KNO_3)_2$;
V) 40% $Cd(NO_3)_2$ + 60% $(RbNO_3)_2$ → $(KNO_3)_2$.

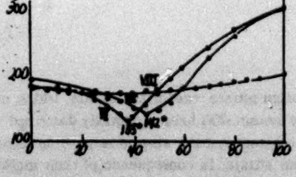

Fig. 5. Sections through ternary system:
VI) 60% $Cd(NO_3)_2$ + 40% $(KNO_3)_2$ → $(RbNO_3)_2$;
VII) 67% $Cd(NO_3)_2$ + 33% $(KNO_3)_2$ → $(RbNO_3)_2$;
VIII) $Cd(NO_3)_2 \cdot RbNO_3$ → $Cd(NO_3)_2 \cdot 2KNO_3$.

Ternary system. The ternary system liquidus surface was investigated along eight sections, the directions of which are shown in Figure 2. Five sections were investigated from the cadmium nitrate—rubidium nitrate side of the triangle with potassium nitrate as a vertex; two sections were studied along the cadmium nitrate—potassium nitrate side with rubidium nitrate as a vertex; the eighth section passed through the chemical compound field.

Equilibrium diagrams for sections I, II, III, IV, and V enable determining lines which bound the cadmium, potassium, and rubidium nitrate crystallization fields.

Sections VI and VII are controls. Section VIII enables establishing the uniformity of the chemical compound field.

Transition points on section equilibrium diagrams and also the corresponding melting points and component compositions are given in the table.

TABLE

Section No.		$Cd(NO_3)_2$	KNO_3	$RbNO_3$	Transition point
		mole %			melting temp.
I	a*	59	30	11	166
	b*	38.7	54	7.3	170
II	a*	59	22	19	160
	b*	39	48	13	164
III	a*	58.5	10	31.5	156
	b*	38.5	40	21.5	159
IV		36.5	27	36.5	138
V		38	8	54	146
VI		37	25	38	155
VII		36.5	16.5	47	142
VIII		No transition point			

a* —composition of first transition point
b* —composition of second transition point

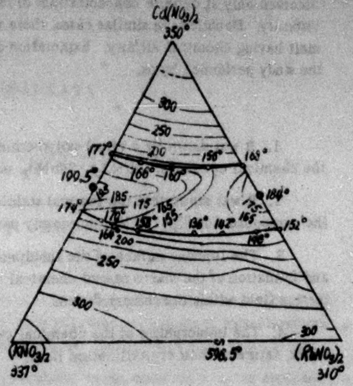

Fig. 6. Base projection of ternary system crystallization surface.

Liquidus curves for the sections are given in Figs. 3, 4, and 5. Experimental data for the ternary system are generalized into a projected isothermal ternary equilibrium space diagram. The isotherms are generally spaced at 50°; in the chemical compound region they are at 10° (Fig. 6).

It can be seen from Fig. 6 that the rubidium nitrate — cadmium nitrate — potassium nitrate ternary system liquidus surface has three crystallization fields: the isomorphic mixture of rubidium and potassium nitrates covering 60.93% of the crystallization area, that of the chemical compounds $Cd(NO_3)_2 \cdot 2KNO_3$ and $Cd(NO_3)_2 \cdot 2RbNO_3$, covering 22.61% of the crystallization area, and cadmium nitrate which covers 16.46% of the crystallization area.

We consider now the chemical compounds $Cd(NO_3)_2 \cdot 2KNO_3$ and $Cd(NO_3)_2 \cdot 2RbNO_3$ which form a single crystallization field. Evidently, rubidium and potassium nitrates, being isomorphic [2], on reacting with cadmium nitrate in the melt form isomorphic chemical compounds — $Cd(NO_3)_2 \cdot 2KNO_3$ and $Cd(NO_3)_2 \cdot 2RbNO_3$, respectively, which on mixture with one another when molten also give a continuous series of isomorphic mixtures (solid solutions). The shape of the Section VIII liquidus curve (Fig. 5), staring from the chemical compound point on the potassium nitrate—cadmium nitrate side of the triangular digram and ending at the chemical compound composition point on the rubidium nitrate—cadmium nitrate side, confirms our discussion.

Because a single field of isomorphic mixtures of the above stated chemical compounds is formed, the ternary system equilibrium diagram has an unusual appearance,—the diagram has a "belt", formed by isomorphic mixtures of the compounds $Cd(NO_3)_2 \cdot 2KNO_3$ and $Cd(NO_3)_2 \cdot 2RbNO_3$ (Fig. 6).

In addition, investigation of the above stated system showed that potassium and rubidium nitrates display a clear tendency to react chemically with cadmium nitrate in melts. Here the tendency toward complex formation is more strongly shown with potassium nitrate than with rubidium nitrate; this follows by comparing the binary system equilibrium diagrams (Fig. 1) and the thermal stability of the given compounds.

Because cadmium nitrate decomposes at temperatures of 318–324°, i.e., below the melting point given in handbook literature*, the melting points of mixtures of components in the cadmium nitrate–rubidium nitrate binary system were measured from 15 to 100% rubidium nitrate. At smaller contents of the latter, the salt melt decomposed with nitrogen dioxide evolution and cadmium oxide formation.

It is characteristic that a transition of the molten salts into the glassy state took place with an enormous viscosity increase in the above stated binary system at a definite rubidium nitrate–cadmium nitrate concentration. Transition of the melt into the glassy state was also observed in the ternary system. This phenomenon was repeatedly observed by us in our earlier investigation of systems of nitrates of metals in the first and second groups of the D.I. Mendeleev periodic table; [1, 2, 3], and moreover, was described by A.P. Rostkovsky [illegible] who investigated the calcium nitrate— potassium nitrate binary system.

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* The melting point given in handbook and periodical literature for cadmium nitrate does not correspond to actuality; this will be shown by us in one of these papers.

In all the cases we previously described, appearance of the glassy state in fused nitrate components was observed only at definite concentrations of the latter, and was always associated with an enormous incrase in viscosity. Doubtless, in similar cases, there will be a genetic viscosity relationship between components in the melt having chemical affinity. Exploration of this relationship particularly represented one of the problems in the study performed by us.

SUMMARY

1. It was shown by a visual-polythermal method of physico-chemical analysis that rubidium nitrate forms the chemical compound $Cd(NO_3)_2 \cdot 2RbNO_3$, melting at 184°, when fused with cadmium nitrate.

2. It was shown that the thermal stability of the complex compound $Cd(NO_3)_2 \cdot 2RbNO_3$ was less than that of the the compound $Cd(NO_3)_2 \cdot 2KNO_3$ previously prepared by us.

3. The liquidus surface of the rubidium nitrate–cadmium nitrate– potassium nitrate ternary system was studied, and formation of the above named chemical compounds was confirmed by the presence of a corresponding crystallization field within the ternary system.

4. The isomorphism of the chemical compounds $Cd(NO_3)_2 \cdot 2RbNO_3$ and $Cd(NO_3)_2 \cdot 2KNO_3$ is discussed, based on the nature of their crystallization field.

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* See Consultants Bureau Translation, p. 1357.

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SODIUM HEXAMETAPHOSPHATE

A. V. Pamfilov and N. M. Dombrovsky

In many respects the oxygen compounds of phosphorus are similar to carbon and silicon compounds, especially in regard to their ability to form polymers. A large number of such polymers are known of metaphosphoric acid, or more accurately, of its salts, of which sodium hexametaphosphate has obtained practical application.

Jones [1] recently gave a method for analyzing a mixture of phosphoric acids, enabling a better approach to the investigation of this unusual product. He determines hexametaphosphate, ortho- and pryophosphate separately and the sum of tri- and tetrapolyphosphates by difference.

The hexametaphosphate is precipitated quantitatively as barium metaphosphate by barium chloride at a pH of the order of 2.5-3, and then ortho-, pyro-, and polyphosphates are precipitated by neutralizing to phenolphthalein. Trimetaphosphate does not precipitate under these conditions, and is determined in the filtrate. Ortho- and pyrophosphates are determined in separate samples after separating the hexametaphosphate [2], the latter by precipitation at pH 4.1 with manganese chloride in presence of acetone. In each of the components, phosphorus is determined by ammonium molybdate, as in determining total phosphorus. Sodium hexametaphosphate was obtained from monosodium phosphate. After dehydration, the monosodium phosphate melts, forming a mobile liquid. To prepare sodium hexametaphosphate, it is necessary to chill this melt rapidly.

Table 1 gives composition constants for products obtained in the temperature interval 620-900° on heating after fusing the starting product for from 10 minutes to 6 hours. The initial product did not fuse below 600°. Heating time and temperature in the stated limits did not affect the yield; this agreees with data of Postnikov and Bronnikov [3]. Also, chilling conditions have no affect, when varied from room temperature to that of solid carbon dioxide (−78.5°). The thermograms were taken with a heating speed of 4° per minute.

TABLE 1

Length of expt. (min.)	Temp. of expt.	P_2O_5 content of product obtained (%)	Composition of product obtained (%)	
			Hexametaphosphate	Trimetaphosphate
30	620-630°	69.5	90.1	9.9
30	720-730	69.5	90.2	9.8
30	820-830	69.4	90.4	9.6
30	870-900	69.5	90.3	9.7
10	620-630	69.3	90.1	9.9
30	620-630	69.5	90.1	9.9
60	620-630	69.4	90.2	9.8
180	620-630	69.5	90.4	9.6
30	870-900	69.5	90.3	9.7
120	870-900	69.4	90.4	9.6
240	870-900	69.4	90.7	9.3
360	870-900	69.2	90.3	9.7

TABLE 2

Temperature		P_2O_5 content in product obtained (%)	Composition of product obtained (%)	
of the melt	of cooling the melt		Hexametaphosphate	Trimetaphosphate
620-630°	*	69.5	90.1	9.9
620-630	0	69.5	90.2	9.8
870-900	*	69.5	90.3	9.7
870-900	0	69.4	90.3	9.7
870-900	−78.5	69.3	90.1	9.9

* Room temperature

Dehydration of monosodium phosphate crystal hydrate takes place in two stages: in the first, a molecule of water splits off between 33-43°, and the second in the 70-80° interval (Fig. 1).

More accurate transition points indicate that these temperatures are equal to 43.5 and 78.5°.

When the second water molecule has split off, a saturated solution of anhydrous monosodium phosphate is

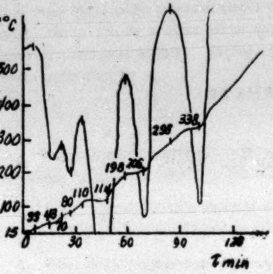

Fig. 1. Thermogram for aqueous monosodium phosphate.

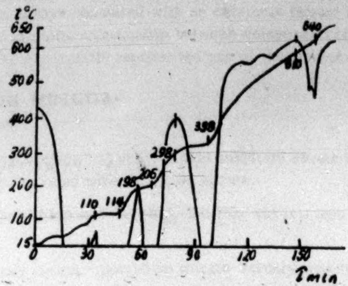

Fig. 2. Thermogram for monosodium phosphate.

formed which on further heating begins to boil at 114°. Subsequently, monosodium phosphate decomposes forming acid pyrophosphate at 198 - 206°. Metaphosphate then is formed in the 298 - 338° interval. Initial melting takes place at 610°.

Sodium metaphosphate undergoes transformation on heating and forms polymetaphospates. It can be seen from Fig. 2 that two endothermal effects take place in the 500 - 600° temperature interval; these are very small in magnitude. To study this process, we increased the differential trace sensitivity; this showed two endothermal transitions in the 500-600° interval. The endothermal effects in Fig. 1 in the 512-560° and 600-608° intervals are connected with dehydrating the hydrated crystals, because they are completely absent in heating the anhydrous product.

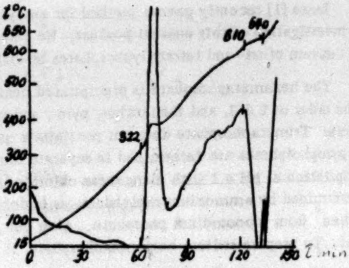

Fig. 3. Thermogram for hexametaphosphate.

Sodium hexametaphosphate, obtained by heating monosodium phosphate in a platinum dish at 630° and containing 90.1% hexametaphosphate and 9.9% trimetaphosphate, was crushed to powder in a porcelain mortar, and heated in a porcelain crucible. In view of the comparatively low specific volume of sodium hexametaphosphate compared to magnesium oxide, titanium dioxide was used as a standard.

The endothermal effect beginning at 322° corresponds to transition of hexametaphosphate into trimetaphosphate.

Analysis of samples heated to 330° for a period of three-five minutes showed that sodium hexametaphosphate was quantitatively transformed into sodium trimetaphosphate; consequently, this effect is not caused, for example, by sintering. At this temperature, sodium hexametaphosphate softens and can be drawn into threads like glass.

On longer heating at this temperature, instead of sodium trimetaphosphate as the main product, other water-insoluble metaphosphates are obtained; the quantity of these increases with increased time of heating. This procedure is suitable for preparing pure trimetaphosphate. At this temperature two processes take place; the first is completed rapidly and corresponds to transition of sodium hexametaphosphate into trimetaphosphate; the second takes place much more slowly and corresponds to transition of trimetaphosphate into other water-insoluble metaphosphates. The endothermal effect in the 614 - 630° interval in Fig. 3, corresponds to fusion of sodium trimetaphosphate, which contained, according to the temperature conditions, some polymetaphospate as an impurity.

Sodium hexametaphosphate does not have a specific melting point and is converted into sodium trimetaphosphate. A number of authors report melting points in the 610 - 640° interval (Bronnikov [4]). Analogous transitions take place with uncrushed sodium hexametaphosphate, although in this case the process occurs much more slowly. Sodium hexametaphosphate hydrolyses markedly, particularly at higher temperatures. For hydrolysis we took a product containing 90.4% sodium hexametaphosphate and 9.6% trimetaphosphate. Hydrolysis of 1 and 2.5% aqueous solutions was performed at 60 and 100°. The samples for analysis were first taken after 24 hours at 60° and after 2 hours at 100°. Hexametaphosphate and trimetaphosphate were determined in the hydrolyzed products. Total remaining phosphate was determined by the difference between total P_2O_5 and the sum of hexametaphosphate and trimetaphosphate (Tables 3 and 4).

TABLE 3

Hydrolysis of 1 and 2.5% Sodium Hexametaphosphate Solutions at 60°

Time of holding sample for analysis (hrs.)	1% solution		2.5% solution	
	Obtained (%)		Obtained (%)	
	Hexametaphosphate	Trimetaphosphate	Hexametaphosphate	Trimetaphosphate
–	90.4	9.6	90.4	9.6
24	88.2	11.7	88.2	11.1
48	84.4	14.7	82.6	12.6
72	–	–	77.1	14.5
96	75.3	17.5	–	–
120	–	–	66.5	19.0
144	68.1	19.8	–	–
168	–	–	60.0	21.8
192	62.0	20.8	–	–
216	–	–	55.2	24.1

TABLE 4

Hydrolysis of 1 and 2.5% Sodium Hexametaphosphate Solutions at 100°.

Time of holding sample for analysis (hrs.)	1% solution		2.5% solution	
	Obtained (%)		Obtained (%)	
	Hexametaphosphate	Trimetaphosphate	Hexametaphosphate	Trimetaphosphate
—	90.4	9.6	90.4	9.6
2	66.0	16.8	64.5	18.3
4	46.9	21.0	42.6	22.5
6	28.2	27.0	25.1	27.4
8	14.3	29.7	9.2	29.9

Sodium hexametaphosphate hydrolyzes in two directions in aqueous solutions. Some of it depolymerizes into sodium trimetaphosphate; this is shown by the increasing quantity of trimetaphosphate; some of it goes to ortho- and other phosphates; this agrees with Bell's conclusions [5].

The hydrolysis rate is sharply dependent on temperature; however, the data obtained do not agree with data of Bronnikov and Bell. Thus, the hydrolysis rate as found by us, particularly at 100°, was much smaller (Table 3 and 4 and Figs. 4 and 5). In these two figures, the percent content of phosphoric anhydride, present as the sodium hexameta-, trimeta-, or total residual phosphate, is plotted along the ordinate; time is plotted along the abscissas axis.

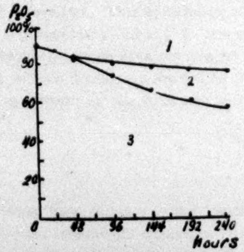

Fig. 4. Hydrolysis of a 1% hexametaphosphate solution at 60°.

1) Trimetaphosphate; 2) total phosphates; 3) hexametaphosphate.*

* No curve 3 appears in the original. Publisher.

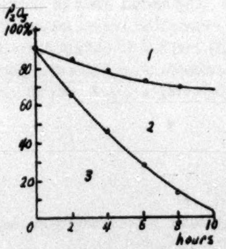

Fig. 5. Hydrolysis of a 1% hexametaphosphate solution at 100°.

1) Trimetaphosphate; 2) total phosphates; 3) hexametaphosphate.*

* No curve 3 appears in the original. Publisher.

The curves give percent phosphate content present with time in the form of sodium hexametaphosphate, sodium trimetaphosphate, and the sum of the other phosphates.

SUMMARY

1. The condition for preparing sodium hexametaphosphate from monosodium phosphate is heating at 620–630° for a 15–30 minute period with rapid subsequent cooling of the melt to room temperature.

2. Pure sodium trimetaphosphate was obtained by heating powdered sodium hexametaphosphate at 330° for a period of three-five minutes.

3. Sodium hexametaphosphate does not have a fixed melting point, because on heating it softens gradually and is transformed into the trimetaphosphate at 330°.

4. Thermographic investigations were performed on monosodium phosphate and on sodium hexametaphosphate over the 15–650° interval.

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OXIDATION OF AQUEOUS SODIUM SULFITE SOLUTIONS BY POSITIVE GASEOUS HYDROGEN, HELIUM, AND OXYGEN IONS

N. A. Goryunova and V.I. Pavlov

The method of oxidizing aqueous sodium sulfite solutions by positive gaseous ions was proposed by V.I. Pavlov in the development of his studies on positive gaseous ions as very vigorous oxidants independent of the nature of the gas [1,2,3,4,5]. The principle of the method consists of the following. When current flows in series through a gas and an electrolyte, gaseous ions on which water vapor condenses are obtained in the gas on discharge (compare with process occurring in Wilson chamber). The solvated ions are directed toward the liquid by the electrical field and enter it. In this, if the electron level of positive gaseous ions (hydrogen, helium and oxygen) carried by the electrical field into the sulfite solution is lower than the electron level of the SO_3^{2-} ions existing in solution, then the positive gaseous ions must react with the SO_3^{2-} ions, for example according to the reaction:

$$SO_3^{2-} + H_2^{+}{}_{\text{from the gas}} \longrightarrow SO_3^{-} + H_2\uparrow \quad .$$

Because of stripping an electron from a SO_3^{2-} ion, it is evident that a product should be formed having a higher degree of oxidation, and thus positive gaseous hydrogen ions, as well as those of other gases, must be oxidants compared to SO_3^{2-} ions.

The oxidation of aqueous sodium sulfite solutions has been studied for a long time by many authors from varying viewpoints. This question occupied Tittoff [6]. A theory for oxidation of aqueous sodium sulfite solutions was proposed by Haber [7]. Haber's conclusions were based on considerably earlier studies by Baubigny [8,9], who showed that when divalent copper ions were introduced into an aqueous sodium sulfite solution in absence of oxygen, sodium dithionate formed in solution and cuprous oxide deposited as a precipitate. Baubigny gave the following scheme for the course of reaction:

$$SO_3^{2-} + Cu^{2+} \longrightarrow SO_3^{-} + Cu^{+}.$$

$$2SO_3^{-} \longrightarrow S_2O_6^{2-}$$

Starting from primary formation of monothionic acid in oxidizing aqueous sodium sulfite solution, Haber gave the following scheme for oxidizing sulfite in presence of oxygen.

$$HSO_3 + O_2 + SO_3^{2-} + H_2O \longrightarrow 2SO_4^{2-} + OH + 2H^{+}. \tag{1}$$

$$OH + SO_3^{2-} \longrightarrow SO_3^{-} + OH^{-}. \tag{2}$$

$$SO_3^{-} + H^{+} \longrightarrow HSO_3 \tag{3}$$

Later, Bäckström [10,11] somewhat modified the oxidation scheme proposed by Haber. Bäckström, not denying HSO_3 formation, proposed the following scheme for sulfite oxidation:

$$SO_3^{-} + O_2 \longrightarrow SO_5^{-}, \tag{4}$$

$$SO_5^{-} + HSO_3^{-} \longrightarrow HSO_5^{-} + SO_3^{-}\text{, etc.} \tag{5}$$

$$HSO_5^{-} + SO_3^{2-} \longrightarrow SO_4^{2-} + HSO_4^{-} \quad . \tag{6}$$

The chain is broken in consequence of the reaction:

$$2SO_3^{-} \longrightarrow S_2O_6^{2-} \tag{7}$$

The presence of dithionate ions, observed in aqueous sodium sulfite solutions after exposure to light in absence of oxygen, also indicates SO_3^{-} formation, because dithionate ions are formed in this case by combination of monothionate ions into dithionate ions.

Here monothionic acid is formed from sulfite ions because of the action of light in removing an electron, which, in its turn, dissociates a water molecule according to the reaction:

$$SO_3^{2-} + H_2O + h\nu_{quant.} \longrightarrow SO_3^{-} + OH^{-} + H.$$

N.A. Shilov [12] appears to be the originator of studies on chain reactions. N.N. Semenov [13] selected in his monograph, as an example of the many types of chain reactions, oxidation of aqueous sodium sulfite solutions, using Haber's theory to explain the process. Later experiments by Gerandes [14] on oxidizing sulfite ions by oxygen led him to deny Haber's theory, since oxidizing sulfite ions with divalent iron ions gave the same effect as did trivalent iron in the Gerandes experiments. According to Gerandes, sulfite oxidation in presence of iron ions takes place on account of oxidation and reduction of iron ions. In absence of oxygen, sulfite oxidizes on account of reducing trivalent iron ions to the divalent form and establishing equilibrium between them.

Generalizing the results of all researchers on oxidizing aqueous sodium sulfite solutions, which are given in the literature, we may conclude that:

a) most workers (Haber, Backström, and others) consider that oxidation of aqueous sodium sulfite solutions, both in presence of catalysts and also by simple photochemical reaction, proceeds via a phase on monothionic acid formation; this is the active center causing reaction;

b) no work was performed using positive gaseous ions as the oxidant.

We studied the reaction of SO_3^{2-} ions, present in aqueous solution, with positive gaseous hydrogen, helium and oxygen ions, directed by an electrical field into an aqueous sodium sulfite solution, in order to explore the processes occurring thereby.

EXPERIMENTAL

1. Electrical equipment. The arrangement of equipment for electrolysis is given in Fig. 1.

A direct current having a potential from 2000 to 3000 V was used for electrolysis. The high potential is necessary to obtain discharge through the gas present in the electrolyzer at atmospheric pressure. The latter was provided for the purpose of eliminating the harmful effect of saturated vapors over the solution, i.e., so that there would be a large quantity of the gas molecules of interest (hydrogen, helium, oxygen) in the gas mixture at the moment of discharge. The discharge took place between the end of a platinum electrode 1 mm diameter) and the electrolyte surface in the closed wide leg of the electrolyzer (Fig. 2.).

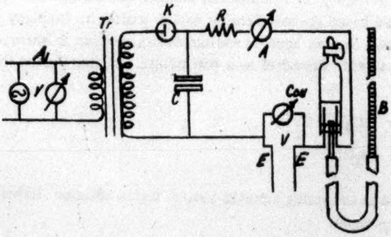

Fig. 1. Arrangement of electrolysis equipment. Tr) transformer for increasing voltage to 2000 - 3000 V; K) kenotron; C) condensor; B) burette; E) electrodes; Cou) Coulometer; A) galvanometer; V) voltmeter; A_1) lighting circuit.

Electrolyzer construction was developed empirically. The separation between the platinum electrode tip and the electrolyte surface, i.e., the "spark" length, was measured by a cathetometer. Because the gaseous ions produced react on their passage through the electrolyte, the gas volume in the electrolyzer continually decreases, and consequently, the "spark" length changes. The spark length was held constant during a test by holding a constant electrolyzer solution level, during this, we determined the quantity of gas evolved from or absorbed by the solution during the test period. Measurements were conducted at atmospheric gas pressure both in the electrolyzer and in the aspirator. The second electrode (0.5 mm diameter) was immersed in electrolyte solution which filled the narrow leg of the electrolyzer and was isolated from the air. The quantity of charge passing through the electrolyzer was calculated from the quantity of oxy-hydrogen gas evolved in the coulometer.

Measurements were performed under atmospheric pressure of oxy-hydrogen gas. For the purpose of controlling constancy of the working equipment, an ammeter was included in the secondary circuit and a volt-meter was located in the primary circuit to establish voltage applied to the transformer. The term "spark", used by us above, is not absolutely precise, because a condition of spark discharge in the gas existed in certain circumstances while in others it was one of a high voltage arc.

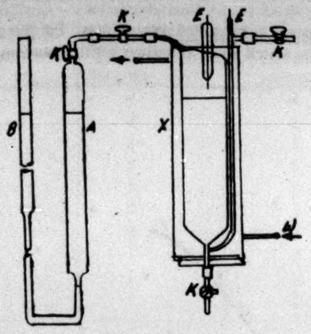

Fig. 2. Electrolyzer arrangement. E) Electrodes; A) gas aspirator; B) burette; K) three-way cock- X) condenser; W) water inlet to condenser.

TABLE 1

Sample No.	Na_2SO_3 concentration	Quantity of gas separated from solu- (H_2), or absorbed by solution (O_2) (ml)	Spark length (mm).
1	1.5 N	194.5	2
2	1.5 N	185.0	2
3	1.5 N	191.0	2
4	1.5 N	238.0	4
5	1.5 N	236.0	4
6	1.5 N	233.0	4
7	0.6 N	111.0	3
8	0.6 N	113.0	3
9	0.6 N	111.0	3
10	1.0 N	167.0	3
11	1.0 N	168.0	3
12	1.0 N	15.0	2
13	1.0 N	14.0	2

In general, all experiments were performed with the electrolyzer shown in Fig. 2, but a portion of the work was performed in an electrolyzer described by V.I. Pavlov [2,3].

2. Experimental Method. In carrying out the experiments with aqueous sodium sulfite solutions, four fundamental variables were subjected to measurement: a) change in volume of the gas serving as a source of gaseous ions: b) quantity of electricity passing through the ionizing gas-electrolyte circuit; c) quantity of sulfite ion disappearing from solution; d) quantity of sulfate ion appearing in solution. In carrying out the experiments, as a rule: a) current strength passed through electrolyte was 5 mA; b) temperature was that of the room (from 20 to 25° C); c) spark length was not more than 3 mm or less than 1.5 mm; d) sodium sulfite solution sulfite concentration varied from 0.6 to 1.5 N.

All the stated values were established in practice based on a whole series of supplementary tests. During these experiments we came upon the fact that certain factors (atmospheric pressure, current strength, spark length, and so on) did not remain constant during the course even of one experiment. Test temperature variation did not exceed $\pm$ 0.5°. Variation in current strength passing through the electrolyte, did not exceed $\pm$ 0.5 mA. Variation in spark length during the period of an experiment did not exceed $\pm$ 0.1 mm.

To explore the effect of the stated factors on sulfite solution oxidation rate, we wet up a whole series of supplemental experiments. It was necessary to do this because of the complete absence of references to this question in the literature.

As a result it was shown that experiments performed at the same conditions were reproducible despite slight inconstancy of certain factors. Discrepancies occurring in experimental results did not usually exceed limits of experimental accuracy, as can be seen from Table 1.

Note 1. The quantity of electricity passing through the electrolyte was determined by the time in which 10 ml oxy-hydrogen gas was evolved in the coulometer in experiments with O_2, and 5 ml in experiments with H_2.

Note 2. Oxygen was used in experiments 1-11. Hydrogen was used in experiments 12-13.

3. Materials. 1. Chemically pure reagents and acids were used in this work. All sulfite solutions were preserved under hydrogen during the entire course of experimentation in order to avoid oxidizing them to sulfate. The sulfites were analyzed for sulfite and sulfate content, and in some cases for free alkali and also approximate hydrogen ion concentration (using selected indicators) in the aqueous sodium sulfite solutions.

2. Of the gases used in the experiments, oxygen and helium were obtained commercially but hydrogen was prepared by action of a caustic soda solution on aluminum turnings followed by a corresponding purification of the gas. All gases were analyzed for contained impurities using the gasometric system of Knorr, Zimin, and Platonov.

Hydrogen, as a rule did not contain more than 3% impurity, of which about 0.5% was oxygen. Helium did not contain oxygen or hydrogen (within the limits of analysis). Oxygen contained about 3.5% nitrogen as an impurity.

DISCUSSION OF RESULTS

I. Explanation of oxidizing tendency of positive gaseous hydrogen, helium, and oxygen ions. For this purpose several series of experiments were performed (Figs. 3 and 4), in which aqueous sodium sulfite solutions were bombarded with gaseous ions — positive, negative, and so on.

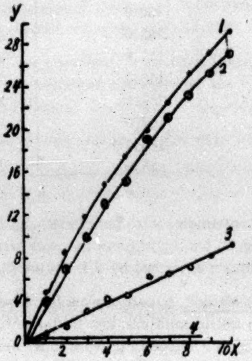

Fig. 3. x) Quantity of oxy-hydrogen gas evolved in coulometer (ml). y) Quantity of H_2 evolved from Na_2SO_3 solution (ml); a) during its bombardment with gaseous hydrogen or helium ions — positive (1 and 2), or negative (3); b) during ordinary hydrolysis (4); c) in experiments with a spark parallel to surface of aqueous Na_2SO_3 solution in electrolyzer (4). 1, 3, and 4) experiments with hydrogen; 2 and 4) experiments with helium.

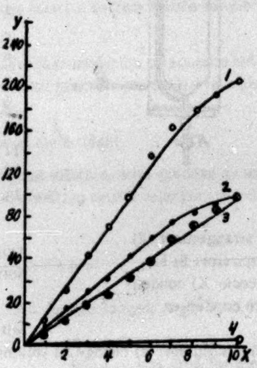

Fig. 4. x) The quantity of oxy-hydrogen gas evolved in coulometer (ml). y) quantity of O_2 absorbed by Na_2SO_3 solution (ml): a) during bombarding solution by gaseous oxygen ions-positive (1), negative (2); b) during ordinary electrolysis (4); c) in experiments with spark parallel to surface of aqueous Na_2SO_3 solution in electrolyzer (3).

It can be seen from the data of Fig. 3 and Fig. 4 that the action of positive gaseous hydrogen, helium, and oxygen ions on a sodium sulfite solution is sharply different from the action of other types of electrolysis and from the action of sparks which are parallel to the sodium sulfite solution surface in the electrolyzer.

The rate of evolving hydrogen from sodium sulfite solution in experiments with positive hydrogen and helium ions and the rate of absorbing oxygen by sodium sulfite solution in experiments with positive oxygen ions was significantly higher than rates in all other series of experiments, and consequently, the rate of sulfite oxidation was also significantly higher. (The relationship between rate of sodium sulfite solution oxidation and the quantity of oxygen absorbed by it or of hydrogen evolved from it during the experiment is given below).

We conclude that positive gaseous hydrogen, helium, and oxygen ions are strong oxidants.

II. Explanation of processes occuring in an aqueous sodium sulfite solution on its bombardment by positive gaseous helium and hydrogen ions.

In the action of positive gaseous hydrogen and helium ions on aqueous sodium sulfite solutions, it was established that: during the period of passing current, continuous hydrogen evolution from solution was observed — gas volume in aspirator continually increased. Independent of the sodium sulfite solution concentration used, the rate of hydrogen evolution from solution remains constant at the beginning of the experiment, and decreases the longer current is passed through the solution (Table 2).

TABLE 2

Experiments with Positive Hydrogen Ions

Oxy-hydrogen gas evolved in coulometer (ml)	Quantity of Hydrogen, evolved by Na_2SO_3 solution (ml) per ml of oxy-hydrogen gas: 0.6 N Na_2SO_3 solution	1.5 N Na_2SO_3 solution
1	4	4
2	3	3
3	3	3
4	3	3
5	3	2
6	2	4
7	2	2
8	1	2
9	1	2
10	1	2

TABLE 3

Quantity of		SO_3^{2-} ions disappearing from Na_2SO_3 solution		
Oxy-hydrogen gas evolved in coulometer (ml)	H_2, evolved from Na_2SO_3 solution (ml)	per ml H_2 evolved	per total H_2 volume evolved	Experiment with
3.0	9.0	$4.45 \cdot 10^{19}$	$4.0 \cdot 10^{20}$	H_2^+
5.8	17.0	$4.42 \cdot 10^{19}$	$7.51 \cdot 10^{20}$	H_2^+
3.0	8.2	$4.68 \cdot 10^{19}$	$3.84 \cdot 10^{20}$	H_2^+
5.9	16.3	$4.71 \cdot 10^{19}$	$7.67 \cdot 10^{20}$	H_2^+
6.0	18.8	$3.48 \cdot 10^{19}$	$6.55 \cdot 10^{20}$	He

TABLE 4

Oxy-hydrogen gas evolved in coulometer (ml)	Quantity of SO_3^{2-} ions disappearing from Na_2SO_3 solution (g $BaSO_4$)	SO_4^{2-} ions forming in Na_2SO_3 solution (g $BaSO_4$)	$\frac{N_{SO_3^{2-}}}{N_{SO_4^{2-}}}$	Experiment with
3	0.155	0.087	1.78	H_2^+
5.8	0.294	0.168	1.75	H_2^+
6	0.254	0.192	1.32	He^+

Reduction in rate is explained by change in initial electrolyte composition in consequence of reactions caused by current. During the course of that interval of time during which from 4 to 6 ml oxy-hydrogen gas was evolved in the coulometer the electrolyzer solution remained transparent, and then, with further passage of current through the solution, the latter gradually developed a slight opalescence which increased and turned to a precipitate. The precipitate, as was established analytically, contained sulfur. At the same time that hydrogen was evolved from the sodium sulfite solution, we observed that SO_3^{2-} ions disappeared from solution (Table 3).

The number of SO_3^{2-} ions disappearing from the sodium sulfite solution (Table 3) is proportional to the number of milliliters of hydrogen evolved from the sulfite solution and is also proportional to the quantity of electricity passing through the electrolyte during the experimental period.

Along with the disappearance of SO_3^{2-} ions from sodium sulfite solution, SO_4^{2-} ions accumulate in solution (Table 4).

$N_{SO_3^{2-}}$ is the number of SO_3^{2-} ions disappearing from the Na_2SO_3 solution:

$N_{SO_4^{2-}}$ is the number of SO_4^{2-} ions forming in the Na_2SO_3 solution.

The number of SO_4^{2-} ions forming in the sodium sulfite solution is proportional to the number of SO_3^{2-} ions disappearing from solution, but is significantly smaller than the latter (Table 4). This difference is greater with positive hydrogen ions than for helium. These facts may evidently be explained by the following considerations.

In working with positive gaseous hydrogen or halium ions, we may assume that oxidation of aqueous sodium sulfite solutions takes place according to the reactions:

$$SO_3^{2-} + H^+_{\text{(from gas)}} \longrightarrow SO_3^- + H. \quad (8)$$

$$SO_3^{2-} + H^+_{2\,\text{(from gas)}} \longrightarrow SO_3^- + H_2\uparrow \quad (9)$$

$$SO_3^{2-} + He^+_{\text{(from gas)}} \longrightarrow SO_3^- + He\uparrow \quad (10)$$

$$SO_3^- + H^+_{\text{(from solution)}} \rightleftharpoons HSO_3 \quad (11)$$

$$HSO_3 + 3H_2O + 2SO_3^{2-} \longrightarrow 3SO_4^{2-} + 2.5H_2\uparrow + 2H^+ \quad (12)$$

The literature indicates possible formation of hypothetical monothionic acid (HSO_3) which does not exist in the free state (Semenov [13], Rais [15], Haber [7], and others).

According to reaction (12), solution acidity should increase (by 0.007 N according to theoretical calculations). It is necessary, naturally, to note that if a small increase in hydrogen ion concentration takes place in solution, then there must be formed at the same time a corresponding quantity of negative ions. In the case in which there is no vapor in solution (in the form of negative ions) for forming hydrogen ions, then the hydrogen ions give up their charge and are evolved as free hydrogen.

Free hydrogen formation takes place in reactions (8), (9), and (12). Hydrogen at the moment of its evolution is a strong reducing agent, and particularly reduces sulfite. Reduction take place variously depending on reaction conditions (length of passing current through sodium sulfite solution, sodium sulfite solution concentration, and so on) either to polythionic compounds or to sulfur, as is shown by analyses.

In using positive gaseous helium ions for oxidation of aqueous sodium sulfite solutions, fewer side reactions can take place, because on neutralizing the positive helium ions (reaction 10), the inert gas evolved does not react with any of the ions present in solution.

Sulfite reduction is possible in this case only on account of hydrogen evolved by reaction 12 or on account of usual cathodic reduction, as also takes place when working with positive hydrogen ions.

In working with helium, this evidently also explains the smaller loss of $SO_3^{=}$ ions from sodium sulfite solution during formation of the same amount of $SO_4^{=}$ ions by passing the same quantity of electricty through the solution and on evolving the same number of milliliters of hydrogen from solution as in experiments with hydrogen.

According to reaction (12), per unit elementary charge introduced from the gas, three $SO_4^{=}$ ions should be formed in solution, and 2.5 molecules of hydrogen should be evolved from solution.

It was shown experimentally, that per elemental charge introduced from the gas into a 1.0 N concentration sulfite solution, 2.7 $SO_4^{=}$ ions were formed and from 2.2 to 2.5 molecules of hydrogen were evolved in the experiments with hydrogen; in the experiments with helium: 2.75 $SO_4^{=}$ ions and 2.2-2.9 molecules of hydrogen.

These data closely approach equation (12) despite its complexity in view of the large number of molecules taking part in the reaction.

Our attempts to find a simpler reaction scheme for oxidizing sodium sulfite by positive gaseous hydrogen and helium ions was not effective. Thus, for example, in the reactions:

$$2HSO_3 + 2H_2O \longrightarrow 2H_2SO_4 + H_2\uparrow \tag{13}$$

or

$$HSO_3 + 2H_2O + SO_3^{=} \longrightarrow 2SO_4^{=} + 2H^{+} + 1.5H_2\uparrow \tag{14}$$

the quantity of $SO_4^{=}$ ions formed in solution and the quantity of free hydrogen evolved, calculated according to equations (13) and (14) do not agree with data obtained experimentally.

III. Explanation of processes taking place in an aqueous sodium sulfite solution during its bombardment with positive gaseous oxygen ions. In action of positive gaseous oxygen ions on an aqueous sodium sulfite solution, it was established that during the period of current passage, continuous oxygen absorption by the solution was observed, such that the aspirator gas volume continually decreased.

Independent of the sodium sulfite solution concentration employed, the rage of oxygen absorption by the solution, which remained more or less constant at the start of the test, decreased with increasing passage of current through the solution (Table 5).

TABLE 5

	Quantity of		
Oxy-hydrogen gas evolved in coulometer (ml)	Oxygen (ml) absorbed by Na_2SO_3 solution per ml oxy-hydrogen gas		
	1.3 N Na_2SO_3 solution	1.0 N Na_2SO_3 solution	1.5 N Na_2SO_3 solution
1	25	19	25
2	25	17	23
3	25	18	20
4	24	17	21
5	29	20	23
6	22	18	19
7	27	17	17
8	24	13	17
9	21	14	17
10	13	14	13

The reduction in rate is explained by change in initial electrolyte composition in consequence of reactions caused by the current. The quantity of oxygen absorbed by the sodium sulfite solution at the start of the experiment is proportional to the quantity of electricity passing through the electrolyte. Preservation of this proportionality depends on many factors (spark length, and so on). Simultaneously with oxygen adsorption by sodium sulfite solution, a disappearance of $SO_3^{=}$ ions from solution was observed (Table 6):

$N_{SO_3^{=}}$ is the number of $SO_3^{=}$ ions disappearing from the Na_2SO_3 solution; N_{O_2} is the number of oxygen molecules adsorbed by the Na_2SO_3 solution.

Along with the disappearance of $SO_3^{=}$ ions from sodium sulfite solution, $SO_4^{=}$ ions accumulate in

TABLE 6

O_2 absorbed by Na_2SO_3 solution (ml)	N_{O_2}	Quantity of SO_3^{2-} ions disappearing from Na_2SO_3 solution: Per ml oxygen absorbed	Per total volume of oxygen absorbed	$\frac{N_{SO_3^{2-}}}{N_{O_2}}$
148	$3.97 \cdot 10^{21}$	$5.30 \cdot 10^{19}$	$7.34 \cdot 10^{21}$	1.98
173	$4.65 \cdot 10^{21}$	$5.37 \cdot 10^{19}$	$9.3 \cdot 10^{21}$	2.00
225	$6.03 \cdot 10^{21}$	$5.16 \cdot 10^{19}$	$11.6 \cdot 10^{21}$	1.92
351	$9.43 \cdot 10^{21}$	$5.26 \cdot 10^{19}$	$18.4 \cdot 10^{21}$	1.95

TABLE 7

Quantity of SO_3^{2-} ions disappearing from Na_2SO_3 solution: g $BaSO_4$	$N_{SO_3^{2-}}$	SO_4^{2-} ions forming in sulfite solution: g $BaSO_4$	$N_{SO_4^{2-}}$	$\frac{N_{SO_3^{2-}}}{N_{SO_4^{2-}}}$
0.637	$1.64 \cdot 10^{21}$	0.600	$1.55 \cdot 10^{21}$	1.06
0.628	$1.78 \cdot 10^{21}$	0.692	$1.79 \cdot 10^{21}$	0.99
0.728	$1.87 \cdot 10^{21}$	0.677	$1.75 \cdot 10^{21}$	1.07
0.784	$2.02 \cdot 10^{21}$	0.760	$1.96 \cdot 10^{21}$	1.03

TABLE 8

Na_2SO_3 solution concentration	Quantity of oxyhydrogen gas, evolved in coulometer (ml)	N_{O_2} per unit elementary charge, introduced from gas	Spark length (mm)
1.5 N	0-3	17	2
	4-6	16	
1.5 N	0-3	18	
	4-6	16	
1.5 N	0-3	21	4
	4-6	18	
1 N	0-3	10	1.7
	4-6	11	
0.6 N	0-3	6	1.7
	4-6	6	
0.1	0-3	1.5	1.7
	4-6	1.5	

solution (Table 7).

$N_{SO_4^{2-}}$ is the number of SO_4^{2-} ions forming in Na_2SO_4 solution.

It can be seen from Tables 6 and 7:

$$(1)\quad \frac{N_{SO_3^{2-}}}{N_{O_2}} \approx 2; \qquad (2)\quad \frac{N_{SO_3^{2-}}}{N_{SO_4^{2-}}} \approx 1.$$

From which we obtain:

$$(3)\quad \frac{N_{SO_4^{2-}}}{N_{O_2}} \approx 2.$$

Consequently, the overall process of oxidizing a sodium sulfite solution by positive gaseous oxygen ions takes place according to the reaction:

$$2Na_2SO_3 + O_2 = 2Na_2SO_4. \qquad (15)$$

Naturally, depending on experimental conditions, N_{O_2} appearing per unit elemental charge introduced from the gas is different (Table 8).

Per unit elementary charge introduced from the gas, in working with positive gaseous oxygen ions, from 1.5 to 20 molecules of oxygen are absorbed (Table 8), and consequently, from 3 to 40 ions of SO_4^{2-} are formed (Formula 3), i.e., the process of sulfite oxidation takes place here as a chain reaction.

Based on the experiments performed, we should regard the oxidation of aqueous sodium sulfite solutions by positive gaseous oxygen ions as the result of several processes:

1) Simple oxygen absorption by aqueous sodium sulfite solution. This process takes place slowly and has almost no effect on the experimental results.

2) Absorption in solution of activated oxygen which forms in the discharge (ozone or atomic oxygen). Formation of activated oxygen in the spark was confirmed both in the experiments with sparks parallel to the solution surface in the electrolyzer and in experiments with negative oxygen ions (Fig. 4.)

3) Direct oxidation of SO_3^{2-} ions by positive gaseous oxygen ions as a result of exchanging their charge with the SO_3^{2-} ions.

For example, according to the reactions:

A) $SO_3^{2-} + O^{+}_{2(\text{from gas})} \rightarrow SO_5^{-}$ and so on, according to Bäckström

(Equations 5, 6)

or B) $SO_3^{2-} + O_{2\,(\text{from gas})}^{+} \rightarrow SO_3^- + O_2$,

$SO_3^- + H^+_{(\text{from solution})} \rightleftarrows HSO_3$, and so on, according to Haber (Equations 1, 2).

4) Combination with oxygen, according to reaction (15), formed from positive gaseous ions after discharging their charge.

The overall process of oxidizing aqueous sodium sulfite solutions, despite the various intermediate reactions, corresponds to reaction (15).

SUMMARY

1. Electrolyzer construction and method of operation were developed.

2. It was shown that the action of positive gaseous hydrogen, helium, and oxygen ions on a sodium sulfite solution is sharply different from the action of other types of electrolysis and from the action of sparks parallel to the Na_2SO_3 solution surface in the electrolyzer.

3. A reaction scheme was proposed according to which positive gaseous hydrogen and helium ions oxidize an aqueous sodium sulfite solution.

4. It was shown that the purest oxidation condition was observed on using positive helium ions as the oxidant, because positive hydrogen ions partially reduce sulfite ions after their neutralization.

5. It was explained that oxidation of aqueous sodium sulfite solutions by positive gaseous oxygen ions takes place as a chain reaction, and the final oxidation result corresponds to the reaction:

$$2Na_2SO_3 + O_2 = 2Na_2SO_4.$$

6. It was shown that positive gaseous hydrogen, helium and oxygen ions are extremely strong oxidants.

7. The method of oxidation by positive gaseous ions is significantly stronger than the method of ordinary electrolysis, and is particularly pure in case inert gases are used.

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REDUCTION OF SILICOTUNGSTATES BY HYDROGEN

VI. METHODS OF ANALYZING SILICOTUNGSTATES AND TUNGSTEN BRONZES

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In our previously published four contributions [1,2,3,4], methods were given for preparing and for carrying out numerous analyses on various potassium silicotungstates and tungsten bronzes. The present paper is devoted to a description of those methods of analysis which were used to establish compositions of silicotungstates, bronzes, and products of their reduction by hydrogen.

Analysis of silicotungstic acid and its salts consisted in determining water, SiO_2, WO_3, K_2O (or Na_2O), and Cl′. Determination of water was by the usual method —drying and ignition to constant weight. The end of ignition was determined by color change in the sample, which acquired a greenish-yellow color of WO_3.

Determination of K_2O. A sample of about 1 g of the substance was dissolved in water and precipitated with quinoline acetate. The precipitant was prepared from 2 ml quinoline, 2 ml concentrated acetic acid, and 100 ml water. After thoroughly washing twice with diluted precipitant, the quinoline silicotungstate precipitate was taken for subsequent SiO_2 and WO_3 determination. The filtrate and wash waters were evaporated; the dry residue gently calcined, converted to K_2SC_4 by addition of H_2SO_4, and finally weighed in the form of this compound.

Determination of SiO_2 and WO_3. The quinoline silicotungstate precipitate was dried in an oven at 80°, and heated and ignited in a porcelain crucible to constant weight.

The SiO_2 and WO_3 oxides obtained were transferred to a platinum or quartz boat and treated with hydrogen chloride in a tube furnace at 600°; WO_3 vaporized as the basic chloride, WCl_2O_2; SiO_2 remained in the boat and was weighed. It is expedient to check the SiO_2 for purity by evaporation with HF + H_2SO_4; WO_3 is determined by difference.

Quinoline silicotungstate is water-insoluble, and consequently, it is very convenient to use it for precipitating heteropolar anions; in some experiments, the complex was precipitated with cinchonine, which also gives an insoluble compound with silicotungstate anions.

In a number of experiments with samples having low K_2O content, the silicotungstate analyses were conducted by another method: the sample of ignited salt following water determination was treated with hydrogen chloride at a 600° temperature; hydrogen chloride volatilizes WO_3; the residue was dissolved in water and filtered from the SiO_2; KCl in the filtrate was titrated by $AgNO_3$ (Mohr method), and SiO_2 was checked for purity by vaporization with HF + H_2SO_4.

In several experiments, a colorimetric method was used for determining SiO_2 quantity based on forming silicomolybdic anions as a result of reaction between SiO_3'' and ammonium paramolybdate. For this a 0.5 g sample of the substance being analyzed was melted in a platinum crucible with 0.3 g sodium acetate. The melt obtained was extracted with 30-40 ml water in a 100-150 ml beaker; the solution was filtered into a 50 ml volumetric flask, brought to the mark and thoroughly mixed. 5-10 ml of the prepared solution was pipetted from the flask and titrated with 2 N HCl to methyl orange; in this manner we established the quantity of HCl necessary to bring the medium to a definite pH in the subsequent colorimetry. Subsequently, a similar 5-10 ml portion of the test solution was taken with a pipette into a tube having dimensions 20 x 2, the quantity of 2 N HCl already established as necessary was added with 0.2 ml excess and thoroughly mixed. After this, 3 ml ammonium molybdate solution was added, the mixture mixed, and the tube set in a steam bath for 5 minutes at 60-70°. After gradual cooling, the solution was poured from the tube into a graduated cylinder or an Egerts tube and colorimetered against a standard solution prepared separately.

Chlorine determination was conducted by an iodometric method developed by Zvenigorodskaya and Gotsdiner [5].

Determination of saponifiable and unsaponifiable alkali in silicotungstate samples which were reduced by hydrogen. A sample weighing 5 to 15 g was wrapped in a packet of dense filter medium and treated in a Soxhlet apparatus with hot water for a period of 5-6 hours. After this treatment, the solution containing SiO_3'', WO_4'', and K_2O was evaporated to dryness and dried in a drying oven at 130-150° (for a period of 3-4 hours) to remove free HCl. The dry residue was treated with hot water and filtered. A residue containing H_2WO_4 and SiO_2 remained on the filter and KCl was found in the filtrate.

The residue was heated in a platinum crucible and then treated with a few drops of H_2SO_4 (density 1.84) and dried on a water bath. The ignited residue of $WO_3 + SiO_2$ was treated with hydrogen chloride and weighed. SiO_2 was checked for purity by vaporization with $H_2SO_4 + HF$, and WO_3 determined by difference. The filtrate, containing HCl, was titrated using 1/20 N $AgNO_3$ (Mohr method).

Determination of oxygen in silicotungstates. A 1 g sample of the substance after water determination was placed in a molybdenum boat and reduced in an electric furnace at a temperature of 800° for a 2.5 hour period (to constant weight) in a dry pure electrolytic hydrogen atmosphere. Oxygen was determined by weight loss.

Analysis of Bronze for Its $K_2O(Na_2O)$ and Tungsten Content

A sample of the substance weighing about 1 g was calcined in a muffle at a 550-600° temperature to constant weight; the tetravalent tungsten of the tungsten bronze was converted to W^{6+}. After calcination, the sample is subjected to hydrogen chloride treatment; as a result of hydrogen chloride action tungsten is quantitatively vaporized as WCl_2O_2; the residue from hydrogen chloride treatment contains potassium (sodium) as chloride, which is titrated using silver nitrate (Wohr method).

In conclusion, we note that methods for analyzing tungsten bronzes for sodium were fully given in the work of V.I. Spitsyn [6]. In 1950, Arne Magneli [7] proposed the following method for analyzing tungsten bronze; WO_3 is vaporized by heating at a temperature of 500° in a stream of hydrogen chloride and oxygen; the bronze forms a residue of sodium chloride. Following solution in water, the quantity of chloride is determined by titration with silver nitrate (by Mohr method). In another variant of the method of analysis, the bronze is decomposed by heating with ammonium persulfate. After treatment by water, the ammonium salt is oxdized with aqua regia; sulfuric acid is removed by heating and evaporating to dryness. Alkali metal ions are isolated on an ion exchanger, regenerated with hydrochloric acid, and determined by argentometry; tungsten is precipitated as its mercuric oxide salt; the oxygen content is determined by decomposing the bronze using an alkaline $K_3[Fe(CN)_6]$ solution and determining its excess iodometrically.

A. Magneli notes that the method proposed by him is not suitable for analyzing tetragonal sodium bronze. As can be seen from the presented description, this foreign method has more limited applicability and is significantly more complicated than the methods which we use in the present paper.

SUMMARY

1. A method for analyzing silicotungstic acid and its salts is described, which consisted in determining water, SiO_2, WO_3, K_2O, Na_2O, and Cl'.

2. A method is proposed for determining saponifiable and unsaponifiable alkali in hydrogen-reduced silicotungstate samples.

3. A method is given for determining oxygen in silicotungstates as well as a method for analyzing bronze for its K_2O and tungsten content.

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COMPLEX FORMATION AND DOUBLE DECOMPOSITION IN THE RECIPROCAL SYSTEM OF SODIUM AND POTASSIUM PYROPHOSPHATES AND MOLYBDATES

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Formation of complex compounds NaX · NaY occurs only seldom in melts obtained in the many binary sodium salt system studied with different anions. Thus, according to literature data [1], only three salts are known ($NaBO_2 \cdot NaPO_3$, $NaBO_2 \cdot Na_4P_2O_7$, and $2NaOH \cdot 3NaI$). There are more compounds of this type for potassim, although, of the three pairs of anions with which sodium forms complex salts, potassium gives one with only one ot them, $KBO_2 \cdot KPO_3$. In studying fusion in the binary system: $(Na_2MoO_4)_2 - Na_4P_2O_7$ and $(K_2MoO_4)_2 - K_4P_2O_7$, it was shown that the sodium salt forms a complex salt, $Na_4P_2O_7 \cdot 2Na_2MoO_4$. The potassium salt did not form an analogous compound.

It was of interest of investigate the behavior of $Na_4P_2O_7 \cdot 2Na_2MoO_4$ within the reciprocal system. In the present work we present results of studying the Na, K‖MoO_4, P_2O_7 reciprocal system on the sides along which the compound $Na_4P_2O_7 \cdot 2Na_2MoO_4$ is formed.

The study was performed by the visual-polythermal fusion method. Platinum crucible. Pt-Pt/Rh thermocouples. All calculations are based on molar per cent. The salts were: potassium pyrophosphate, obtained by decomposing chemically pure dipotassium phosphate; potassium molybdate – by fusing chemicallly pure K_2CO_3 with freshly prepared MoO_3, taken in stoichiometric proportions. MoO_3 was obtained from $(NH_4)_2MoO_4$ by calcining the latter. The MoO_3 obtained was held at 600° in a stream of air for a period of several hours. Sodium pyrophosphate and sodium molybdate were of the c.p. grade. Melting points of the salts were: $K_4P_2O_7$–1095°, $Na_4P_2O_7$–992°; Na_2MoO_4–690°, K_2MoO_4–926°.

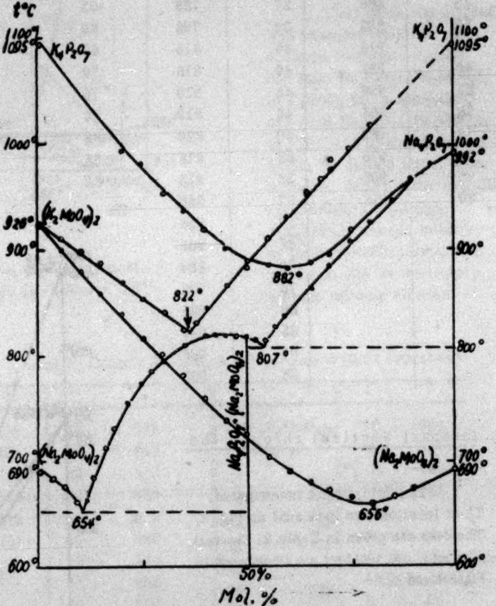

Fig. 1. Binary sets in the Na, K‖MoO_4, P_2O_7 reciprocal system.

Binary Sets

1) $(K_2MoO_4)_2 - (Na_2MoO_4)_2$. Studied by Amador [1]. Our data (Fig. 1) – a solid solution with a minimum of 21% K_2MoO_4 and 656°. 2) $(K_2MoO_4)_2 - K_4P_2O_7$, (Table 1, Fig. 1) – eutectic. The eutectic is at 36% $K_4P_2O_7$ and 822°. 3) $K_4P_2O_7 - Na_4P_2O_7$ studied by Amador [1]. Our data are given in Fig. 1. 4) $(Na_2MoO_4)_2 - Na_4P_2O_7$ (Table 1, Fig. 1) forms the chemical compound $Na_4P_2O_7 \cdot 2Na_2MoO_4$, with a congruent melting point at 820°. Intersection points: E_1 at 10% $Na_4P_2O_7$ and 654°; E_2 at 54% $Na_4P_2O_7$ and 807°.

Diagonal Sections

1) $(K_2MoO_4)_2 - Na_4P_2O_7$ (Table 1, Fig. 2). 2) $(Na_2MoO_4)_2 - K_4P_2O_7$ (Table 1, Fig. 2)

TABLE 1

Binary Systems and Diagonal Sections

A) Initial component; b) added component. Column 1 gives mol. % B; Column 2 gives the temperature at which crystals first appear.

1	2	1	2	1	2	1	2
A—$(K_2MoO_4)_2K_4P_2O_7$—B		A—$(Na_2MoO_4)_2Na_4P_2O_7$—B		A—$(K_2MoO_4)_2Na_4P_2O_7$—B		A—$(Na_2MoO_4)_2K_4P_2O_7$—B	
0	926	0	690	5	902	3	680
5	911	3	684	10	870	6	658
10	898	6	674	15	845	10	655
15	888	9	663	20	813	12	695
20	870	11	663	25	774	15	732
25	854	13	684	30	752	20	766
30	842	15	714	35	728	25	792
35	825	17.5	732	40	732	30	803
38	830	21	756	45	738	35	804
40	845	24	774	50	743	40	806
45	866	27	786	55	742	45	792
50	883	30	796	60	737	50	743
55	910	35	810	65	753	55	734
60	932	40	818	70	776	60	758
65	956	45	819	75	802	65	787
68	968	48	819	80	832	70	826
70	982	50	820	83	852	75	869
71	978	52	816	85	857	80	918
75	995	54	815	88	884	85	969
80	1018	57	826				
		59	836				
		66	865				
		70	884				
		75	906				
		80	926				
		85	946				
		90	966				
		95	982				

Internal Sections through the System

19 sections were investigated. Their locations are indicated on Fig. 3. The data are given in Table 2. Several characteristic sections are illustrated in Figs. 2 and 4.

Projection of the reciprocal system space diagram onto the composition square indicates formation of 5 crystallization fields in the system: 1) the compound field, occupying 30.71% of the system crystallization surface area and the solid solution fields: 2 3) for $Na_4(K_4)P_2O_7$ and 4, 5) for $Na(K_2)MoO_4$ (Fig. 5) which decompose into their components within the system. The compound

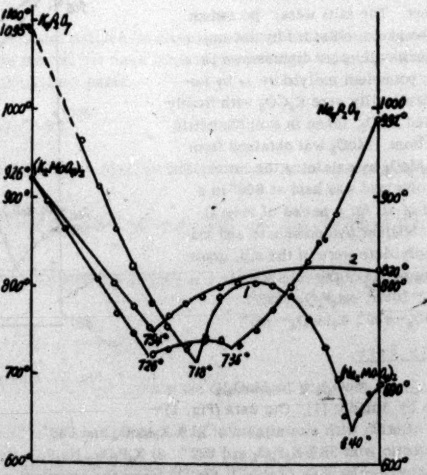

Fig. 2. Diagonal sections from $(K_2MoO_4)_2$ to $Na_4P_2O_7$ and from $K_4P_2O_7$ to $(Na_2MoO_4)_2$.
1) Compound $Na_4P_2O_7 \cdot (Na_2MoO_4)_2$; 2) stable non-diagonal section from $(Na_2MoO_4)_2 \cdot Na_4P_2O_7$ to $(K_2MoO_4)_2$.

field intersects both diagonal sections. The only stable section in the system is the non-diagonal section from $Na_4P_2O_7 \cdot (Na_2MoO_4)_2$ to $(K_2MoO_4)_2$, the eutectic point of which, at 754°, seems transitional. The latter was confirmed by projecting the reciprocal system crystallization surface onto the $K_2MoO_4 - Na_2MoO_4$ side (Fig. 6), and onto the $(K_2MoO_4)_2 - K_4P_2O_7$ side (Fig. 7). It follows from Figs. 5, 6, and 7 that there are 2 ternary eutectic points and one ternary transition point, compositions for which are given in Table 3.

The system was divided into triangles using two non-diagonal sections: a stable one from $Na_4P_2O_7 \cdot (Na_2MoO_4)_2$ to K_2MoO_4 and a non-stable* one from $Na_4P_2O_7 \cdot (Na_2MoO_4)_2$ to $K_4P_2O_7$. The stated sections divide the system into 3 phase triangles. Melts in the $Na_4P_2O_7 \cdot (Na_2MoO_4)_2 - (Na_2MoO_4)_2 - (K_2MoO_4)_2$ triangle solidify at final crystallization of the system at 635° at the ternary eutecic mixture E_1; melts

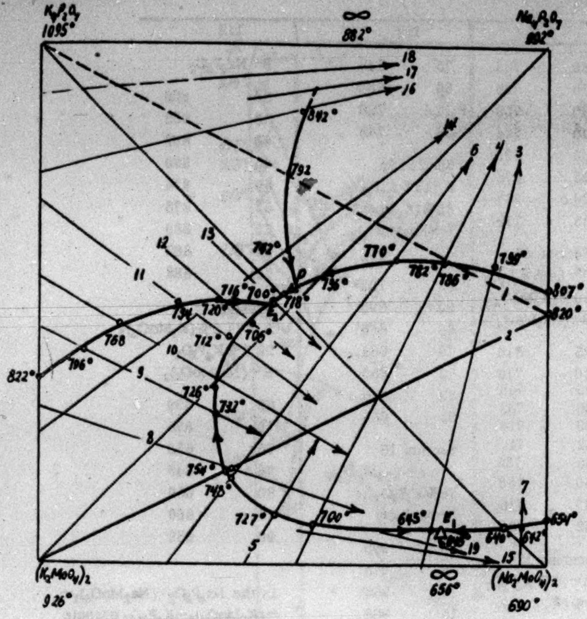

Fig. 3. Crystallization surface in the Na, K ‖ MoO_4, P_2O_7 reciprocal system and locations of sections studied. E_1 - 635; E_2 - 698; P - 720°.

TABLE 2

A) Initial mixture; B) added component; Column 1 - mol.%; Column 2 - temperature of first crystals appearance

1	2	1	2	1	2	1	2	1	2	1	2
Section 1 A —		60	828	60	772	20	782	50% $(K_2MoO_4)_2$		70	824
50% $(Na_2MoO_4)_2$		65	858	65	758	25	802	B — $Na_4P_2O_7$		75	854
50% $Na_4P_2O_7$		70	886	70	781	30	816	0	720	P_1 8	700
B — $K_4P_2O_7$		P_1** 16.5	786	75	810	35	826	5	712	P_2 59.5	782
0	820	P_2 52	792	80	832	40	819	10	714		
5	810			E*** 64	754	45	816	15	752	Section 5	
10	800	Section 2				50	814	20	775	A — 60% $(K_2MoO_4)_2$	
15	789	A — 50%		Section 3		55	806	25	793	40% (Na_2MoO_4)	
20	793	$(Na_2MoO_4)_2$		A — 25%		60	802	30	805	B — $Na_4P_2O_7$	
25	798	50% $Na_4P_2O_7$		$(K_2MoO_4)_2$		65	816	35	812	0	758
30	792	B — $(K_2MoO_4)_2$		75% $(Na_2MoO_4)_2$		70	836	40	808	3	753
35	792	0	820	B — $Na_4P_2O_7$		75	862	45	803	6	743
40	792	25	820	0	660	P_1 7.5	645	50	797	9	732
45	792	45	802	5	658	P_2 58.5	799	55	792	12	746
50	792	50	794	10	692	Section 4		60	780	15	760
55	814	55	788	15	742	A — 50% $(Na_2MoO_4)_2$		65	806	20	782

* The non-stable non-diagonal section is shown in Fig. 5 as a dashed line.

** Crystallization path intersection point.

*** Eutectic.

TABLE 2 — (continued)

1:2	
25	796
P10	727

Section 6
A—75% $(K_2MoO_4)_2$
25% $(Na_2MoO_4)_2$
B—$Na_4P_2O_7$

0	818
6	800
12	768
15	754
20	768
25	778
30	794
35	802
40	806
45	804
50	800
55	795
60	774
65	785
70	796
75	816
80	848
P_1 16.5	748
P_2 59	770

Section 7
A—5% $(K_2MoO_4)_2$
95% $(Na_2MoO_4)_2$
B—$Na_4P_2O_7$

0	680
2	671
4	664
6	658
10	700
12	723
8	642

Section 8
A—30% $K_4P_2O_7$
70% $(K_2MoO_4)_2$
B—$(Na_2MoO_4)_2$

0	832
5	826
10	818
15	812
20	806
25	792
30	782
35	762
40	752
45	758
50	760
55	753
60	742
65	730
P38	748

Section 9
A—45% $K_4P_2O_7$
55% $(K_2MoO_4)_2$
B—$(Na_2MoO_4)_2$

0	868
3	856
6	836
9	812
12	784
15	772
20	764
25	757
30	750
35	732
40	758
45	774
P_1 9	796
$P_2$35	732

Section 10
A—55% $K_4P_2O_7$
45% $(K_2MoO_4)_2$
B—$(Na_2MoO_4)_2$

0	910
5	870
10	830
15	783
20	763
25	758
30	747
35	729
40	742
45	764
50	775
$P_1$16	768
$P_2$34.5	727

Section 11
A—70% $K_4P_2O_7$
30% $(K_2MoO_4)_2$
B—$(Na_2MoO_4)_2$

0	975
5	935
10	902
15	844
20	800
25	746
30	733
35	725
40	752
45	774
50	790
55	806
$P_2$26.5	734
$P_2$38	712

Section 12
A—80% $K_4P_2O_7$
20% $(K_2MoO_4)_2$
B—$(Na_2MoO_4)_2$

25	810
30	770
33	748
36	732
39	714
42	710
45	735
50	758
$P_2$37	716
$P_2$42	706

Section 13
A—95% $K_4P_2O_7$
5% $(K_2MoO_4)_2$
B—$(Na_2MoO_4)_2$

35	747
40	720
45	702
50	732
55	748
P 45.5	700

Section 14
A—25% $K_4P_2O_7$
75% $(K_2MoO_4)_2$
B—$Na_4P_2O_7$

0	856
5	842
10	822
15	803
20	784
25	768
30	747
35	728
40	736
45	742
50	752
55	774
60	788
65	807
70	826
75	849
80	884
$P_2$35.5	720
$P_2$48	742

Section 15
A—15% $K_4P_2O_7$
85% $(K_2MoO_4)_2$
B—$(Na_2MoO_4)_2$

50	716
55	702
60	690
65	676
70	666
75	660
80	656
85	660

Section 16
A—25% $(K_2MoO_4)_2$
75% $K_4P_2O_7$
B—$Na_4P_2O_7$

0	995
5	974
10	954
15	936
20	914
25	896
30	882
35	868
40	862
45	854
50	844
55	848
60	852
65	864
52	842

Section 17
A—17.5% $(K_2MoO_4)_2$
82.5% $K_4P_2O_7$
B—$Na_4P_2O_7$

40	870
45	860
50	850
55	848
60	854
65	860
70	868

Section 18
A—10% $(K_2MoO_4)_2$
90% $K_4P_2O_7$
B—$Na_4P_2O_7$

30	920
35	902
40	892
45	880
50	876
55	875
60	880
65	882
70	888

Section 19
A—77.5% $(K_2MoO_4)_2$
22.5% $K_4P_2O_7$
B—$(Na_2MoO_4)_2$

65	699
70	675
75	658
78.5	648
80	650
85	660
90	669

in the $Na_4P_2O_7 \cdot (Na_2MoO_4)_2$—$(K_2MoO_4)_2$—$K_4P_2O_7$ triangle similarly solidify at the ternary eutectic mixture E_2 at 698°. The other triangle — $Na_4P_2O_7 \cdot (Na_2MoO_4)_2$—$Na_4P_2O_7$—$K_4P_2O_7$ — does not include a eutectic point, and its melts solidify at 720° in a transition point.

The K, Na ‖ MoO_4, P_2O_7 reciprocal system is a clear example of the effect of complex formation on the double decomposition reaction. A stable chemical compound $Na_4P_2O_7 \cdot (Na_2MoO_4)_2$ is formed in the system. Unfortunately, absence of data on heat of formation of the components or of the compound makes impossible the performance of energy calculations. It is probable, though, that the compound heat of formation is greater than the heat of reaction

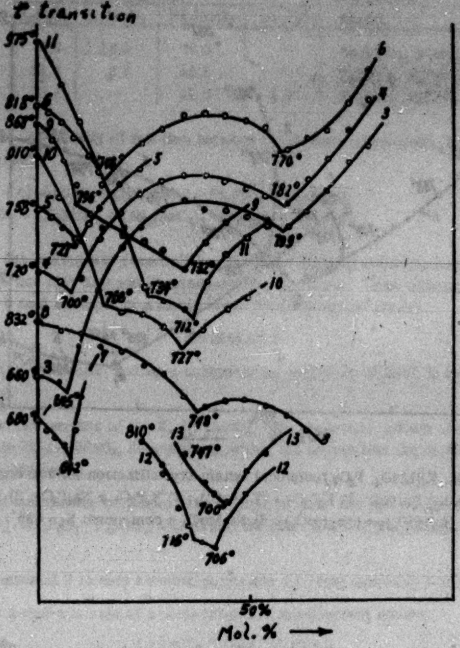

Fig. 4. Typical sections in the Na, K$\|$MoO$_4$, P$_2$O$_7$ reciprocal system.

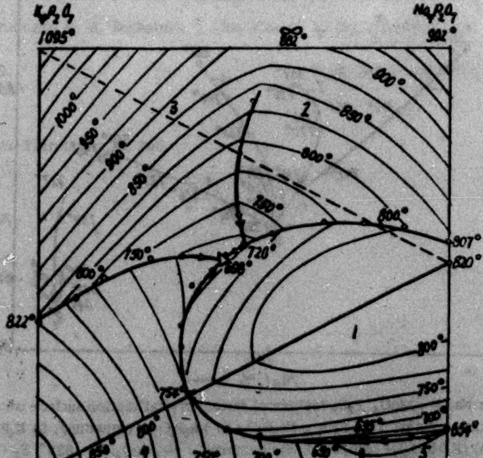
$K_4P_2O_7$
1085°
882°
$Na_4P_2O_7$
982°
1000°
950°
900°
850°
800°
3
2
780°
807°
820°
720°
708°
750°
822°
1
800°
750°
752°
700°
654°
650°
4
5
$(K_2MoO_4)_2$
926°
655°
$(Na_2MoO_4)_2$
690°

Fig. 5. Projection of the Na, K$\|$MoO$_4$, P$_2$O$_7$ reciprocal system space diagram onto the composition square. 1) Na$_4$P$_2$O$_7$·(Na$_2$MoO$_4$)$_3$, 2,3) Na$_4$(K$_4$)P$_2$O$_7$ field; 4,5) Na$_2$(K$_2$)MoO$_4$ field.

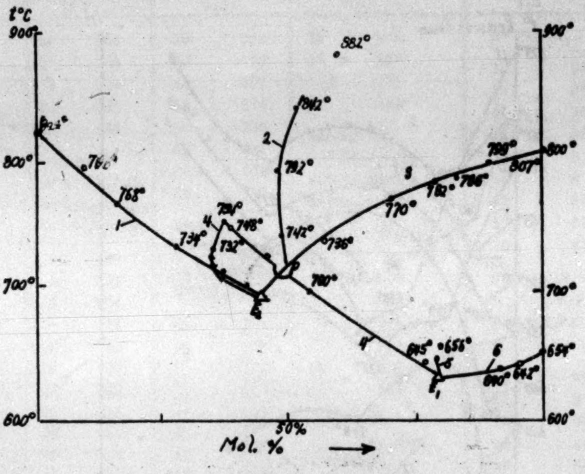

Fig. 6. Projection of the Na, K$||$MoO$_4$, P$_2$O$_7$ reciprocal system crystallization surface onto the K$_2$MoO$_4$—Na$_2$MoO$_4$ side. Crystallization curves: 1) $K_4P_2O_7$ + $(K_2MoO_4)_2$; 2) $K_4P_2O_7$ + $Na_4P_2O_7$; 3) $Na_4P_2O_7$ + compound; 4) K_2MoO_4 + compound; 5) $(K_2MoO_4)_2$ + $(Na_2MoO_4)_2$; 6) Na_2MoO_4 + compound; E$_1$ - 635°; E$_2$ - 698°; P - 720°.

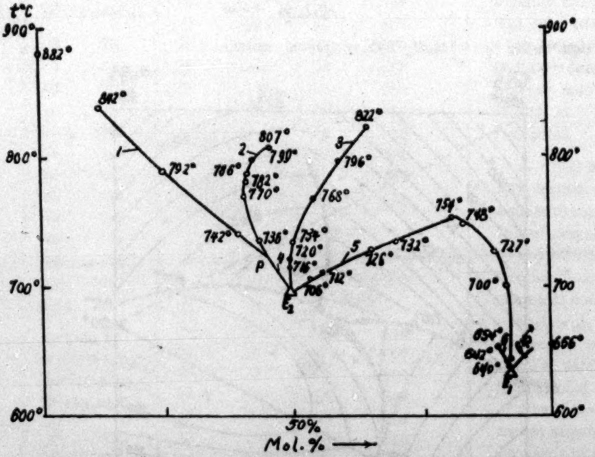

Fig. 7. Projection of the Na, K $||$MoO$_4$, P$_2$O$_7$ reciprocal system crystallization surface onto the $(K_2MoO_4)_2$—$K_4P_2O_7$ side. Crystallization paths: 1) $K_4P_2O_7$ + $Na_4P_2O_7$; 2) $Na_4P_2O_7$ + compound; 3) $K_4P_2O_7$ + (K_2MoO_4); 4) $K_4P_2O_7$ + compound; 5) $(K_2MoO_4)_2$+ compound; 6) compound + Na_2MoO_4; E$_1$ - 635°; E$_2$ - 698°; P - 720.

TABLE 3

Point	Temperature	Composition (Mol. %)				Equilibrium phases
		$K_4P_2O_7$	K_2MoO_4	Na_2MoO_4	$Na_4P_2O_7$	
Eutectic E_1	635°	7.5	14.5	78.0	–	Na_2MoO_4, K_2MoO_4, compound
Eutectic E_2	698	51.0	3.5	45.5	–	K_2MoO_4, $K_4P_2O_7$, compound
Transitional Pt	720	50.0	–	45.0	5.0	$Na_4P_2O_7$, $K_4P_2O_7$, compound

for double decomposition. As a result of reaction between the starting components, either case leads to forming the chemical compound:

$$K_4P_2O_7 + 4Na_2MoO_4 = (Na_2MoO_4)_2 \cdot Na_4P_2O_7 + 2K_2MoO_4$$
$$2Na_4P_2O_7 + 2K_2MoO_4 = (Na_2MoO_4)_2 \cdot Na_4P_2O_7 + K_4P_2O_7$$

Triangulation of the system was accomplished using two sections radiating from the compound field. The diagonal sections did not play any part in triangulating the system. Thus, according to A. G. Bergman's classification [2], this is a real example of a semi-reversible non-diagonal system.

SUMMARY

1. A 1:1 chemical compound, having a congruent melting point of 820°, is formed in the $Na_4P_2O_7$–$(Na_2MoO_4)_2$ binary system.

2. The crystallization surface of the K, Na $\|$ MoO_4, P_2O_7 reciprocal system consists of a field for solid solutions of $Na_4(K_4)P_2O_7$ in $Na_2(K_2)MoO_4$, decomposing within the system into the components, and a field for the $(Na_2MoO_4)_2 \cdot Na_4P_2O_7$ compound.

3. The reciprocal system was subjected to triangulation using two non-diagonal sections. The triangulating section $(Na_2MoO_4)_2 \cdot Na_4P_2O_7$–$K_2MoO_4$ was stable; the other section, $(Na_2MoO_4)_2 \cdot Na_4P_2O_7$–$K_4P_2O_7$, was not stable.

4. The system constains 2 ternary eutectic points and 1 ternary transition point.

5. The system is a real example of a semi-reversible non-diagonal system.

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[2] A. G. Bergman and G. A. Bukhaleva, J. Gen. Chem., 20 (2), 235 (1950).*

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* See Consultants Bureau Translation, p. 245.

STUDY OF COMPLEX FORMATION IN TERNARY SYSTEM SOLUTIONS BY METHODS OF PHYSICO-CHEMICAL ANALYSIS.

V. THE SYSTEM: $SbBr_3-AlBr_3-C_6H_5Cl$

E. Ya. Gorenbein

In studying the $SbBr_3-AlBr_3-C_6H_5Cl$ system [1] by the electrical conductivity method it was shown that the binary systems $SbBr_3-C_6H_5Cl$ and $AlBr_3-C_6H_5Cl$ conduct almost no current. However, the ternary system $SbBr_3-AlBr_3-C_6H_5Cl$ is a current conductor. The appearance of conductivity in systems consisting of components which do not conduct current in their individual liquid states is explained by the formation of current conducting complexes.

Investigation of this system was performed in such a way that the molecular ratio between aluminum bromide and chlorobenzene remained constant, changing the concentration of antimony bromide. However, we were not able to establish the composition of the compound formed in solution despite the fact that the molecular ratio of $SbBr_3$ to $AlBr_3$ somewhat exceeded an equimolar mixture of these components.

Thus, for a molecular ratio of $AlBr_3$ to C_6H_5Cl equal to 0.102, the molecular ratio of $SbBr_3$ to $AlBr_3$ attained 2.387; with a molecular ratio of $AlBr_3$ to C_6H_5Cl of 0.23, the molecular ratio of $SbBr_3$ to $AlBr_3$ attained 1.874; and with molecular ratios of $AlBr_3$ to C_6H_5Cl equal to 0.35 – 0.36, the highest molecular concentration ratio of $SbBr_3$ to $AlBr_3$ reached 1.39, and even on the specific electrical conductivity-composition curves there were none of the special characteristic cusps by which one could judge the composition at which a complex formed in solution.

Naturally, it was of interest to study this system using a modified method for changing the concentration of system components in such a manner that one component, used as a solvent, should remain constant, and that concentrations of the remaining two should change according to such a rule that the sum of their gram-molecules should remain constant.

EXPERIMENTAL

Initial materials and method of working. Aluminum bromide and antimony bromide were prepared and stored in the very manner which was described in our previous paper [2]. Chlorobenzene after careful purification was dried over fused calcium chloride and distilled into an elongated tube which was immediately sealed when filled. In this work we used a preparation distilling at constant temperature. Solutions of appropriate concentration were prepared in a conical flask with side-tube. The calculated quantity of chlorobenzene was added from a burette to the $AlBr_3-SbBr_3$ melt. The C_6H_5Cl quantity added was checked by weighing. To preserve the solutions from traces of moisture, the burette (25 ml) communicated with the air through a calcium chloride tube filled with drying agent.

After filling the vessels for electrical conductivity, viscosity and pycnometry with the solutions, the tubes were placed in a water thermostat and were taken for test after passage of some time. Variation of thermostat temperature did not exceed ±0.1°.

Electrical conductivity was measured using a lamp generator and optical indicator [3].

Electrical conductivity, viscosity, and density. The $SbBr_3-AlBr_3$ system was studied in the liquid state for fusibility [4], electrical conductivity [5, 6], and viscosity [6] over the full range of concentrations. According to these data, the electrolyte is a complex having the composition $SbBr_3 \cdot AlBr_3$.

Electrical conductivity of this same system was studied in a variety of organic solvents (benzene, toluene, nitrobenzene, ethylene bromide, and so on) which form compounds with components present in the given complex. Chlorobenzene does not form a compound either with $SbBr_3$ [7] or with $AlBr_3$ separately. This significantly eases solving the question on electrolyte composition in solution and together with this makes possible explanation of the than the $SbBr_3 + AlBr_3$ concentration, which we knew. Thus the coefficients were equal to: $\alpha = 1.930 \cdot 10^{-2}$ and $\beta = 4.143 \cdot 10^{-2}$, where the temperature coefficient was calculated for the temperature interval from 15 to 20° for the 0.2 isomolar concentration, and where the concentration coefficient was calculated for a temperature of 20° and for a range of isomolar concentrations from 0.2 to 0.3. We expect that further study will make it possible to establish interrelations between these coefficients.

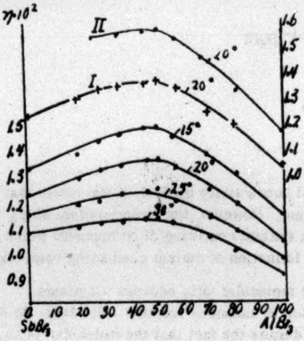

Fig. 1. Dependence of $SbBr_3 - AlBr_3 - C_6H_5Cl$ system viscosity on ratio of antimony bromide to aluminum bromide.
(I) 0.2 Isoconcentration; (II) 0.3 isoconcentration.

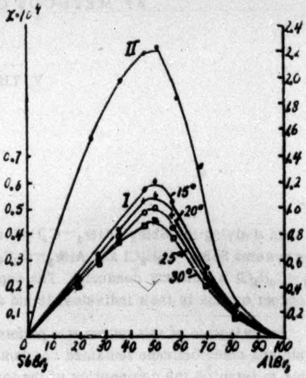

Fig. 2. Dependence of specific electrical conductivity on antimony bromide : aluminum bromide concentration ratio at 20°.
(I) 0.2 Isoconcentration; (II) 0.3 isoconcentration at 20°

The Fig. 2 curves give the dependence of specific electrical conductivity on ratio of antimony bromide concentration to that of aluminum bromide. The conductivity maximum indicates the composition of the electrolyte forming in solution. As with the viscosity data, so also for electrical conductivity — the complex composition in solution is expressed by the formula: $SbBr_3 \cdot AlBr_3$.

The curves marked with a Roman numeral I were constructed from data at an isomolar concentration of 0.2, while the curves marked with a Roman numeral II are for isomolar concentrations equal to 0.3. The numbers on the right hand ordinate axis refer to curves II.

The effect of temperature and concentration on system conductivity is shown in Fig. 2. With increase in temperature, the specific electrical conductivity decreases somewhat (curves I). This, evidently, is explained by decomposition of the current-conducting complex into its constituent components. Increase in concentration, i.e., transition to a higher isomolar concentration for the $SbBr_3 + AlBr_3$ components leads to a significant increase in solution conductivity. This is connected with significant increase in degree of association of the electrolyte forming in solution.

As is known, in solvents with a small D_n, with increase in electrolyte concentration, its degree of association increases; together with this, the solution electrical conductivity increases. Thus, for example, increase in concentration of the $SbBr_3 \cdot AlBr_3$ complex in aluminum bromide as a solvent leads to an increase in its molecular weight; at a concentration of 2.76% the molecular weight is 668, and at 22.52% it is equal to 1850 [9]; along with this, the electrical conductivity also increases [5, 6]. Conductivity of this complex in a benzene solution, at concentrations at which its molecular weight is equal to its formula weight according to cryoscopic data, is very small. Thus, with a 15% concentration of complex in benzene, its molecular weight is close to its formula weight and its electrical conductivity is equal to $0.8 \cdot 10^{-7}$ mho [10]. With increase in concentration, molecular weight increases and so does solution conductivity. This is in complete agreement with the law for reducing corrected molar electrical conductivity in diluting high concentration solutions [11].

effects of dilution and temperature on system viscosity changes. For this purpose, we studied electrical conductivity, viscosity, and density of the stated system at two isomolar concentrations, equal to 0.2 and 0.3, and at 15, 20, 25, and 30°.

Results of measurements at a 20° temperature are given in Tables 1 and 2; the other data are given graphically.

TABLE 1

Molecular ratio $\frac{SbBr_3 + AlBr_3}{C_6H_5Cl} = 0.2$

Temperature 20°

$\frac{SbBr_3 + AlBr_3}{C_6H_5Cl}$ (Moles)	Mol. % $AlBr_3$	d_{40}^{t}	$\eta \cdot 10^2$	$\kappa \cdot 10^4$
0.1989	100	1.3749	1.034	–
0.2003	81.05	1.4092	1.180	0.110
0.2004	70.31	1.4288	1.241	0.252
0.1999	57.37	1.4506	1.333	0.474
0.1998	50.58	1.4628	1.361	0.549
0.2006	46.15	1.4704	1.352	0.524
0.2004	36.15	1.4886	1.342	0.409
0.200	28.38	1.4989	1.329	0.312
0.1995	19.19	1.5088	1.299	0.233
0.1992	0	1.536*	1.226*	–

TABLE 2

Molecular ratio $\frac{SbBr_3 + AlBr_3}{C_6H_5Cl} = 0.3.$

$\frac{SbBr_3 + AlBr_3}{C_6H_5Cl}$ (Moles)	Mol. % $AlBr_3$	d_4^{t}°	$\eta \cdot 10^2$	$\kappa \cdot 10^4$
0.2999	100	1.4811	1.159	–
0.2977	81.78	1.5271	1.319	0.259
0.2994	68.08	1.5621	1.449	1.129
0.3000	58.90	1.5838	1.526	1.843
0.3005	51.51	1.6041	1.558	2.223
0.3008	46.41	1.6136	1.548	2.181
0.2969	36.50	1.6303	1.541	1.976
0.3011	25.77	1.6631	1.536	1.553

Variation of system viscosity with ratio of components ($SbBr_3$ to $AlBr_3$) for the two isomolar concentrations 0.2 and 0.3, during which the total number of gram molecules of these components was taken as 100 mol.%, is shown in Fig. 1. Isothermal curves for 15, 20, 25, and 30° characterize the variation in system viscosity for an isomolar concentration equal to 0.2.

For a graphical presentation we compare two curves in this figure; I – for an isoconcentration equal to 0.2 at a 20° temperature, and II – for the very same temperature at an isoconcentration of 0.3. The scale on the right-hand ordinate axis remains the same, but numerical values have been shifted upward somewhat for convenience. It can be clearly seen from the data presented that decreasing concentration or increasing temperature leads to reducing system viscosity, although naturally to varying degrees.

If one compares $SbBr_3-AlBr_3$ system viscosity in the molten state [6] with our data for the ternary system, then it is completely clear that addition of an indifferent solvent gradually reduces system viscosity, i.e., the largest viscosity will be observed at that time when the complex forming in the system appears in the pure liquid state under otherwise equal conditions. Such a picture was observed by N. Kurnakov and I. Kvyat [8] in their study of the aniline-allyl mustard oil-toluene ternary system. This kind of study should furnish material for theoretical calculations of the effect of an indifferent solvent or temperature on system viscosity, if either its dependence on temperature is known or if the dependence of system viscosity on indifferent solvent added is known.

Since the viscosity curve maxima correspond to an equimolar composition for the compound forming in solution, we calculated the temperature and concentration viscosity coefficients for this electrolyte according to the formulas:

$$\alpha = \frac{\eta_{t_2} - \eta_{t_1}}{\frac{\eta_{t_2} + \eta_{t_1}}{2} \cdot (t_2 - t_1)}; \qquad \beta = \frac{\eta_{c_1} - \eta_{c_2}}{\frac{\eta_{c_1} + \eta_{c_2}}{2} \cdot \left(\frac{1}{C_1} - \frac{1}{C_2}\right)}.$$

For our isomolar concentrations of 0.2 and 0.3, in consequence of reaction between the components $SbBr_3$ and $AlBr_3$ to form a complex having the composition $SbBr_3 \cdot AlBr_3$, concentration of the latter was smaller by 2-fold

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* The numbers marked with asterisks were obtained by extrapolating data for the $SbBr_3-C_6H_5Cl$ binary system measured at temperatures of 35, 40, and 45°; (at lower temperatures crystalline $SbBr_3$ separates).

In conformity with this law, the highest system electrical conductivity would correspond to the corrected electrical conductivity of the individual liquid electrolyte. This state corresponds to the highest degree of association [9]. Depending on the amount of dilution, the degree of association decreases, electrical conductivity falls, and the electrical conductivity maximum becomes more sloped; at a molecular electrolyte state corresponding to the molecular weight $SbBr_3 \cdot AlBr_3$, in solvents with small D_n, the conductivity is smallest. The maximum is almost levelled off. In solvents with large D_n, this point corresponds to a minimum molecular electrical conductivity. Further dilution of these solvents leads to electrolytic dissociation of the neutral ion pairs according to the laws of dilute solutions and the molecular weight here will already be less than the formula weight.

A consequence resulting from the laws of high concentration electrolytic solutions to the effect that the electrolyte in solution should be observed at its lowest conductivity in the monomolecular state, was confirmed by us for other electrolytes in various solvents.

SUMMARY

1. Viscosity, electrical conductivity, and density of the $SbBr_3$–$AlBr_3$–C_6H_5Cl system were studied over the entire range of $SbBr_3$ and $AlBr_3$ concentrations, at two isomolar concentrations and at varying temperatures.

2. It was shown that the use of our method for studying ternary systems gives more satisfactory data for judging the composition of complex compounds forming in solution.

3. It was established that the reason for appearance of conductivity in this system was the formation of a complex compound having the composition $SbBr_3 \cdot AlBr_3$.

4. It was shown that maximum conductivity was reduced on transition from a higher isoconcentration to a lower one, and that reduction in degree of association of the electrolyte was in full agreement with the law for decrease in corrected molecular electrical conductivity of high concentration electrolyte solutions on dilution.

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VAPOR-LIQUID PHASE EQUILIBRIA IN THE P_2O_5–H_2O SYSTEM

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A mixture is formed on thermal degradation of orthophosphoric acid, or by its reaction with phosphoric anhydride, which contains various phosphoric acids: orthophosphoric, H_3PO_4; pyrophosphoric, $H_4P_2O_7$; triphosphoric acids: orthophosphoric-$H_5P_3O_{10}$; and metaphosphoric acids having the general formula $(HPO_3)_n$. We will call such a mixture "strong phosphoric acid".

Mutual transformations of the stated acids, except for polymerized metaphosphoric acids, take place rather rapidly; consequently, the ratio of acids in the mixture is determined by the total phosphoric anhydride content and does not depend on the method by which the mixture was prepared [1, 2, 3], if formation of polymerized metaphosphoric acids is excluded. From this it follows that vapor pressure in the P_2O_5–H_2O system is uniquely determined by the liquid phase phosphoric anhydride content (with the above stated reservation).

Data published in the literature on variation of vapor pressure over phosphoric acids with temperature and composition [4-8] covers a wide range of phosphoric anhydride content. However, these data are limited – up to a pressure of only one atmosphere. Results of measuring vapor pressure over phosphoric acids at pressures of one atmosphere and higher are presented below.

Method of Measurement

Measurements were performed in an apparatus (Fig. 1), a novel feature of which was use of the liquid whose vapor pressure was being determined as a manometric fluid in a differential manometer. A U-shaped tube was used for this; its narrow arm was closed and filled with liquid at the start. Liquid level in the open arm was thus lower than its level in the closed arm (in selecting the difference in levels it is necessary to consider liquid expansion on heating). Inert gas pressure, measured with a manometer, was maintained over the liquid in the open arm. Subsequently, the U-tube was gradually heated. At some particular temperature a bubble of vapor is formed in the closed arm. At this moment, saturated vapor presses on the liquid in the closed arm and inert gas presses on the liquid in the open arm. On further increase in temperature, the liquid level in the closed arm decreases with a simultaneous rise in level in the open one. The levels are equal at equilibrium between the saturated vapor pressure and the inert gas pressure. The manometer reading directly gives the liquid vapor pressure corresponding to the temperature at which the levels are equal. For increasing measurement accuracy, one should proceed slowly close to this temperature. Since the vapor phase volume is small, its formation does not involve significant change in liquid composition. Measurements at atmospheric pressure were conducted in a pyrex glass tube; here air was used as the inert gas. Heating was provided by an air thermostat or by a bath containing a molten mixture of KNO_3 and $NaNO_2$. The moment the levels were equal was fixed by direct observation.

Our tests of a number of materials showed that copper was significantly more resistant to the action of strong phosphoric acid at high temperatures than various grades of steel, bronze, brass, and other alloys. Consequently, a tube prepared from a red copper ore (cuprite), was used for measurements at pressures above atmospheric. A molten mixture of KNO_3 and $NaNO_2$ was used for heating. The differential manometer null position in this case was determined by closing a contact employing the rather high electrical conductivity of phosphoric acid.

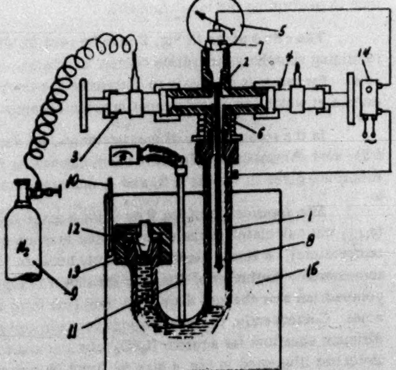

Fig. 1. Equipment arrangement for determining vapor pressures over phosphoric acids at pressures greater than 1 Explanation (of symbols) is given in text.

Apparatus construction is shown in Fig. 1. The copper U-tube 1, filled with phosphoric acid of known composition, was connected to manifold 2, on which were mounted two fine-regulating small gas valves 3, 4, a precision manometer 5 (one scale division was equal to 0.1 atm), a water cooling coil 6, and an airplane engine spark plug used for introducing electrode 7. A copper wire, insulated by a porcelain sleeve along its entire length, served as electrode 8 and was soldered to the spark plug. The bare end of the wire was placed at the zero level. The moment contact was made by the acid touching the bare electrode end was indicated by the signal lamp of electronic relay 14. The apparatus is connected to a compressed nitrogen cylinder 9 by valve 3. Valve 4 is used for regulating pressure. Temperature is measured by thermometer 10 immersed in bath 15 and by thermocouple 11 mounted on the measuring tube. For convenience in filling the measuring tube with acid, the seal on the short arm was made using a conical plug 12 and union-nut 13. To establish the necessary difference in levels, excess acid was removed from the open arm by connecting the tube to an evacuated tube via a glass capillary set at the zero level.

Strong phosphoric acid was prepared by heating crystalline orthophosphoric acid (analytically pure) with previously distilled phosphorous pentoxide in a pyrex glass flask at 180° for a 8-50 hour period until the solution was completely homogeneous Samples were analyzed for total phosphoric anhydride by a gravimetric procedure – precipitation of phosphoric anhydride using ammonium molybdate [9], by a method of potentiometric titration with quinhydrone and calomel electrodes [10], and by directly titrating a sample of acid being analyzed after first boiling it in water – using thymolphthalein.

The difference between results determined by the several methods did not exceed 0.5% P_2O_5. The samples prepared contained from 29 to 80 weight% phosphoric anydride.

Results of Measurement

The first series of measurements involved determining the temperature at which the vapor pressure over phosphoric acid was equal to 1 atm. The low volatility of phosphoric acid enables assuming that the gas phase over it consists almost entirely of water vapor up to temperatures of 350-380°. According to Brown and Whitt [8], the gas phase over phosphoric acid contains 0.47 wt. % P_2O_5 at 300° and 1.96 wt % P_2O_5 at 385°. On this basis, we may assume that the values obtained by us for vapor pressures over phosphoric acids correspond to the water vapor pressure. Measurement results are given in Table 1 and illustrated graphically in Fig. 2.

It should be particularly noted that a singular point is present on the composition – temperature isobar (Fig. 2.) which corresponds to transition from aqueous orthophosphoric acid solutions to strong phosphoric acid. Phosphoric anhydride content at this point corresponds to the formula H_3PO_4. This fact was not noted in any of the earlier papers on determining vapor pressures in the P_2O_5-H_2O System.

In Fig. 2 we compare literature data on dependence of phosphoric acid composition on temperature at constant vapor pressure with results from the present study The data of the several authors agree very well for orthophosphoric acid solutions. Our data are somewhat different from literature values for strong phosphoric acid; this, evidently, is explained by the difference in methods used in performing the measurements.

The curve given in Fig. 2 may be used for determining phosphoric anhydride content of phosphoric acids. For this it is necessary to determine the temperature at which test sample vapor pressure becomes equal to atmospheric pressure.

TABLE 1

Dependence on Liquid Phase Composition of Temperature at which Vapor Pressure was 1 atm in P_2O_5 - H_2O System.

Wt. % P_2O_5	Temperature	Wt. % P_2O_5	Temperature
29.0	103°	73.2	290°
50.7	123°	74.0	297°
53.5	130°	74.5	301°
57.5	141°	74.7	304
65.9	180°	76.3	318°
67.6	200°	77.8	335°
69.8	220°	78.7	350°
70.7	240°	79.0	355°
71.7	260°	80.0	380°
72.4	284°		

In the second series of measurements, we determined vapor pressure dependence on temperature for constant acid compositions using seven samples having P_2O_5 contents ranging from 69.8 to 76.3 wt. % Measurement results are given in Tables 2, 3, and 4, and are presented graphically in Fig. 3.

The dependence of log P on $\frac{1}{T}$ for a given composition, and likewise that of log a_{H_2O} on $\frac{1}{T}$, is not linear (a_{H_2O} was calculated as the ratio of vapor pressure over phosphoric acid to the vapor pressure of water at the same temperature). A linear dependence exists between log P and phosphoric anhydride content of the acid at constant temperature. Isotherms of this type are shown in Fig. 4. The slope angle of the straight lines with respect to the composition axis changes sharply on transition from aqueous orthophosphoric acid solutions to strong phosphoric acids. Consequently, the relationships between composition, vapor pressure, and temperature must be expressed by different equations for aqueous H_3PO_4 solutions and for a strong phosphoric acids. For strong phosphoric acids, isotherms illustrated in Fig. 4 may be fitted by equations of the form:

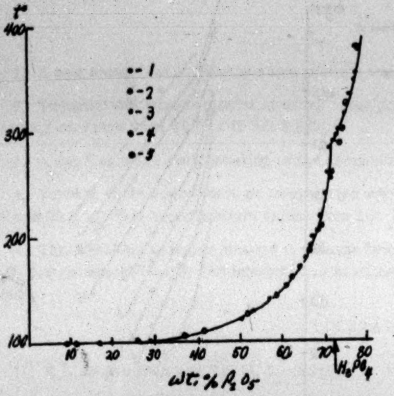

Fig. 2. 1 atm Pressure Isobar for the P_2O_5-H_2O System. Data sources: 1) Ours; 2) I. Kablukov and K. Zagvozdkin [4]; 3) E. Britske and N. Pestov [5]; 4) Brown and Whitt[8].

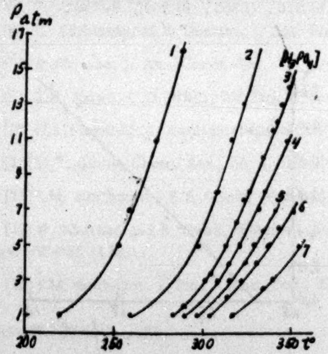

Fig. 3. Dependence of phosphoric acid vapor pressure on temperature. P_2O_5 content: 1) 69.8; 2) 71.7; 3) 72.4; 4) 73.2; 5) 74.0; 6) 74.7; 7) 75.3.

TABLE 2

Dependence of Aqueous Orthophosphoric Acid Solution Vapor Pressure on Temperature.

Weight % P_2O_5	Temperature	Vapor Pressure (atm).
69.8	220°	1.0
	253°	5.0
	260°	7.0
	275°	11.0
	290°	16.0
71.7	260°	1.0
	298°	5.0
	309°	8.0
	318°	11.0
	325°	13.0
	345°	20.0

TABLE 3

Dependence of Orthophosphoric Acid Vapor Pressure on Temperature (72.4% P_2O_5).

Temperature	Vapor Pressure (atm).
284°	1.0
290°	1.5
302°	3.0
305°	3.4
214°	5.0
320°	6.3
325°	7.6
327°	8.0
335°	10.0
341°	11.5
343°	12.0
346°	13.0
350°	14.0

$$\log \frac{P}{P_0} = -k\Delta C, \quad (1)$$

where: P is the pressure of water vapor over acid of the given composition; P_0 is the pressure of water vapor over pure H_3PO_4 (i.e., at 72.4 wt. % P_2O_5) at the same temperature; k is a coefficient depending on temperature; ΔC is the difference between water contents of H_3PO_4 and strong phosphoric acid, expressed in weight percent: ΔC = 27.6 − wt. % H_2O = wt. % P_2O_5 − 72.4.

Values of k calculated by equation (1) are given in Table 5; values of P and P_0 used in the calculations were obtained by graphical interpolation of data in Tables 3 and 4.

A plot of k versus 1/T gives a straight line (Fig. 5) which corresponds to the equation:

$$k = \frac{500}{T} - 0.671. \quad (2)$$

TABLE 4

Dependence of Strong Phosphoric Acid Vapor Pressure on Temperature

Wt. % P_2O_5	Temperature	Vapor pressure, atm	
		Experimental	According to Equation (3)
73.2	290°	1.0	1.0
	309	3.0	2.9
	315	4.0	3.8
	322	5.0	5.0
	332	7.0	7.0
	336	8.0	7.8
	348	10.8	10.5
74.0	297	1.0	1.1
	316	3.0	2.8
	325	4.0	4.2
	330	5.0	4.9
	335	5.8	5.7
	342	7.0	7.0
74.7	304	1.0	1.1
	315	2.1	2.0
	323	3.0	2.9
	331	4.0	3.9
	338	5.0	4.9
	344	6.0	5.9
	352	7.0	7.3
76.3	318	1.0	1.2
	335	2.5	2.6
	340	3.1	3.1
	355	5.0	5.1

Equations (1) and (2) give:

$$\log \frac{P}{P_0} = \left(0.671 - \frac{500}{T}\right) \Delta C. \qquad (3)$$

Experimental values of vapor pressure over strong phosphoric acid are compared with values calculated from Equation (3) in Table 4. The discrepancies do not exceed experimental error. Thus, Equation (3) may be used as an interpolation equation for calculating strong phosphoric acid vapor pressures.

Equation (3) expresses a linear dependence of log P on P_2O_5 weight percent at constant temperature. Weight percents were used for convenience in calculation; an analogous dependence would be obtained in the given composition range by expressing composition in mole fraction. This kind of dependence is observed in other systems. Thus, for example, the logarithm of HCl vapor pressure (or the logarithm of HCl activity) over concentrated aqueous solutions varies approximately linearly with solution composition, as can be easily demonstrated by examining the corresponding data [12]. These relation-

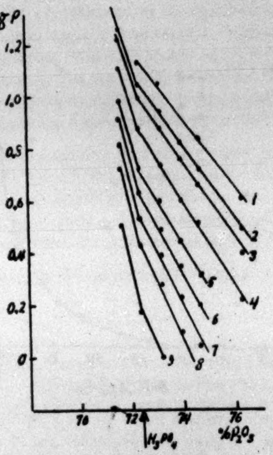

Fig. 4. Isotherms of log pressure versus composition at given temperatures.

1) 350°, 2) 340°, 3) 335°, 4) 325°, 5) 315°, 6) 310°, 7) 305°, 8) 300°, 9) 290°.

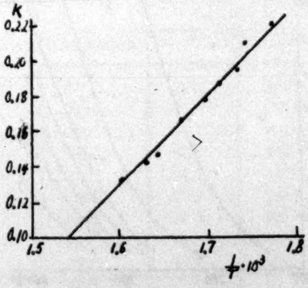

Fig. 5. Dependence of coefficient k on T.

TABLE 5

Temperature Dependence of k

Temperature	k	Temperature	k
290	0.2201	325	0.1662
300	0.2101	335	0.1470
305	0.1945	340	0.1440
310	0.1866	350	0.1331
315	0.1780		

ships can be regarded as a generalization of I. M. Sechenov's law [13].

SUMMARY

1. A new method for measuring vapor pressure was developed.

2. Temperatures were measured at which vapor pressures in the P_2O_5-H_2O system were equal to 1 atm in the composition range from 29.0 to 80 wt.% P_2O_5.

3. A singular point, corresponding to the compound H_3PO_4 (72.4% P_2O_5) was found on the isobar.

4. Vapor pressure dependence on temperature was measured for acids having P_2O_5 compositions ranging from 69.8 to 76.3 wt. % at vapor pressure values from 1 to 20 atm.

5. The logarithm of vapor pressure is a linear function of water content for strong phosphoric acids (i.e., for P_2O_5 content above 72.4%). An interpolation equation is given for calculating vapor pressure of strong phosphoric acids.

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THE SYSTEM: $BeSO_4-FeSO_4-H_2O$

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In the present work, we made an investigation of a system containing beryllium sulfate, ferrous sulfate, and water, in order to explore the nature of the interaction of these salts. It was known from literature data that ferrous sulfate forms solid solutions with sulfate salts of many divalent metals (magnesium, zinc, cadmium, cobalt, nickel and copper). According to data of Klatso [1], ferrous sulfate forms double salts with beryllium sulfate. Our studies of the $BeSO_4$-$FeSO_4$-H_2O system were performed at 25 and 60°. The 60° temperature was selected by us because of the condition that ferrous sulfate and beryllium sulfate crystallize as tetrahedra at this temperature, and thus the possibility of forming mixed crystals of these salts would not be excluded. Composition of the third phase was determined by Shreinemakers' residue method and also on the basis of crystallo-optical analysis. Solutions and solid phase were analyzed for iron content by a chromatometric method, the beryllium-iron sum was determined by an alkalimetric method, and the quantity of beryllium calculated from the data obtained. Solution refractive index was measured with an Abbe refractometer. Solution density was determined using pycnometers.

Investigation of the System: $BeSO_4$-$FeSO_4$-H_2O at 25°.

Refractive indexes for the solid phase of the system under study at 25° are given in Table 1, as determined by us using an immersion method; refractive indexes for $BeSO_4 \cdot 4H_2O$ and $FeSO_4 \cdot 7H_2O$ are noted (taken by us from Winchell's handbook).

TABLE 1.

Refractive index of solid phase (Tests 1,2,3-Table 2)		Refractive index for $BeSO_4 \cdot 4H_2O$ (according to Winchell)	
Ng	Np	Ng	Np
11471	1.440	1.472	1.439
Refractive index of solid phase (Tests 5,6,7,8,9,Table 2)		**Refractive index for $FeSO_4 \cdot 7H_2O$ (according to Winchell)**	
Ng	Np	Ng	Np
1.489	1.471	1.486	1.471

By comparaing data obtained by us with refractive index values taken from Winchell's handbook for the sulfate salts of beryllium and ferrous iron, we may conclude that the solid phase was $BeSO_4 \cdot 4H_2O$ in experiments 1,2, and 3 (Table 2) and was $FeSO_4 \cdot 7H_2O$ in experiments 5,6,7,8, and 9 (Table 2). Table 2 and Fig. 1 present results of investigating liquid and solid phase compositions in the $BeSO_4$-$FeSO_4$-H_2O system at 25°.

TABLE 2.
System: $BeSO_4$-$FeSO_4$-H_2O (25°)

Experiment number	Liquid phase composition (wt. %)			"Residue" composition (wt. %)			4)Bottom phase
	$BeSO_4$	$FeSO_4$	H_2O	$BeSO_4$	$FeSO_4$	H_2O	
1	28.72	—	71.28	—	—	—	$BeSO_4 \cdot 4H_2O$
2	25.53	3.59	70.88	54.52	0.50	44.98	
				51.00	1.13	47.87	
3	24.11	6.54	69.35	—	—	—	
4	24.00	8.09	67.91	39.42	13.25	47.33	$BeSO_4 \cdot 4H_2O$ + + $FeSO_4 \cdot 7H_2O$
				65.14	15.84	19.02	
5	21.31	10.72	67.97	—	—	—	$FeSO_4 \cdot 7H_2O$
6	17.19	11.60	71.21	1.20	51.45	47.35	
				2.15	49.60	48.25	
7	12.23	14.17	73.60	0.96	51.58	47.46	
				1.02	50.76	48.22	
8	5.73	18.39	75.88	0.50	54.04	45.46	
9	—	22.74	77.26	—	—	—	

Liquid phase densities, refractive indexes and compositions for this same system are given in Table 3. As is shown by the Fig. 2 data, solubility, density, and refractive index isotherms for the solutions consisting of two branches, corresponding to equilibrium of solutions with the salts $BeSO_4 \cdot 4H_2O$ (branches A_1B_1; $A'_1B'_1$; $A''_1B''_1$) and $FeSO_4 \cdot 7H_2O$ (branches B_1C_1; $B'_1C'_1$; $B''_1C''_1$).

$BeSO_4$-$FeSO_4$-H_2O system at 60°. Ferrous sulfate solutions oxidize very rapidly at elevated

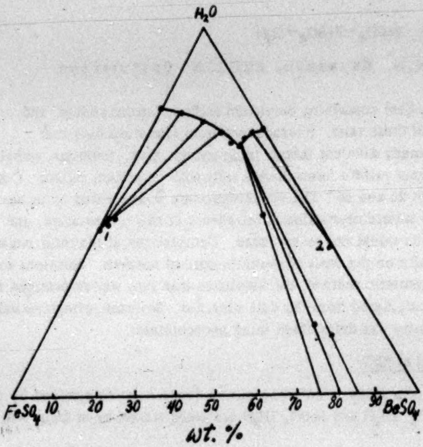

Fig. 1. System $BeSO_4-FeSO_4-H_2O$ at 25°.
1 $-FeSO_4 \cdot 7H_2O$; 2 $-BESO_4 \cdot 4H_2O$.

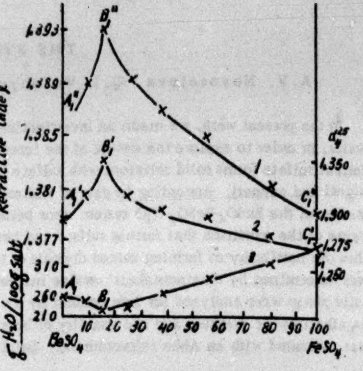

Fig. 2. System $BeSO_4-FeSO_4-H_2O$ at 25°.
1) Refractive index isotherm; 2) density isotherm; 3) solubility isotherm.

temperature. A continuous stream of hydrogen was passed through the solution in order to guard against oxidation. Stability of ferrous sulfate solutions was noticeably increased in presence of beryllium sulfate. System equilibrium was reached after mixing the solution with excess solid phase for 8-10 hours. Control experiments were performed over a 48 hour period. Solid phases were investigated by Shreinemaker's "residual" method.

TABLE 3.
System: $BeSO_4-FeSO_4-H_2O$ at 25°.

Experiment number	d_4^{25}	Liquid phase refractive index	Salt composition (%)		Quantity of water in g per 100 g salt
			$BeSO_4$	$FeSO_4$	
1	1.285	–	100	–	248.0
2	1.306	1.389	89.06	10.94	243.4
3	–	–	83.93	16.07	226.2
4	1.340	1.393	82.97	17.03	211.7
5	1.312	1.389	73.64	26.36	212.3
6	1.300	1.387	59.84	40.16	247.4
7	1.296	1.385	42.57	57.43	278.8
8	1.282	1.882	19.95	80.05	314.7
9	1.270	1.378	–	100	339.7

Compositions of solution and solid phases investigated are given in Table 4.

Solubility isotherms in the system at 60° (Fig. 3) consist of 2 branches, corresponding to crystallization from solution of a solid phase consisting of $BeSO_4 \cdot 4H_2O$ and $FeSO_4 \cdot 4H_2O$; no double salts or solid solutions were observed at 60°.

SUMMARY

1. Solubility, density, and refractive index isotherms were investigated for the $BeSO_4-FeSO_4-H_2O$ system at 25 and 60°.

2. It was established that ferrous sulfate and beryllium sulfate decrease each other's solubility.

3. Existence of double salts and solid solutions was not observed in the system.

TABLE 4

System: $BeSO_4-FeSO_4-H_2O$ (60°)

Test No.	Liquid phase composition, wt. %			"Residue" composition, wt. %			Bottom phase
	$BeSO_4$	$FeSO_4$	H_2O	$BeSO_4$	$FeSO_4$	H_2O	
1	–	34.94	65.06	–	1) 65.73 2) 66.70	34.27 33.30	$FeSO_4 \cdot 4H_2O$
2	8.82	25.56	65.62	0.69	61.48	37.83	
3	13.58	21.05	65.37	1) 0.5 2) 0.4	1) 63.0 2) 63.2	36.5 36.4	
4	14.56	20.60	64.84	–	–	–	
5	20.20	16.68	63.12	1) 18.14 2) 18.15	1) 43.00 2) 43.18	38.86 38.67	$FeSO_4 \cdot 4H_2O$ + $BeSO_4 \cdot 4H_2O$
6	20.40	16.70	62.90	14.62	49.11	36.27	
7	20.42	16.50	63.08	35.80	17.88	46.32	
8	34.60	–	65.40	1) 57.04 2) 58.80	– –	42.96 41.20	$BeSO_4 \cdot 4H_2O$
9	27.21	6.60	66.19	1) 51.68 2) 52.10	1) 1.11 2) 1.11	47.21 46.79	
10	26.70	7.75	65.55	1) 51.12 2) 51.30	1) 1.90 2) 2.01	46.98 46.69	
11	23.68	10.38	65.94	–	–	–	

4. The solid phases were crystal hydrates of simple salts: $BeSO_4 \cdot 4H_2O$ and $FeSO_4 \cdot 7H_2O$ at 25°; $BeSO_4 \cdot 4H_2O$ and $FeSO_4 \cdot 4H_2O$ at 60°.

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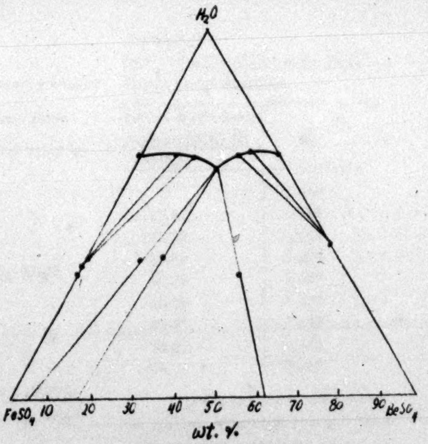

Fig. 3. $BeSO_4-FeSO_4-H_2O$ at 60°.
1) $FeSO_4 \cdot 4H_2O$; 2) $BeSO_4 \cdot 4H_2O$.

SYSTEM $BeSO_4 - MnSO_4 - H_2O$ (25°)

O.I. Vorobyeva and L.R. Osanova

In the present work, we conducted an investigation of an aqueous system containing beryllium sulfate and manganese sulfate, for the purpose of explaining the nature of interaction of these salts.

According to literature data, manganese sulfate forms solid solutions with sulfates of many divalent metals (iron [1], zinc [2], and magnesium [2,3]).

It is noted in a paper by Klatso [4] that manganese sulfate forms mixed crystals of two types with beryllium sulfate: triclinic crystals containing 23.1% MnO and 2.73% BeO; and tetragonal crystals containing 8.41% MnO and 10.44% BeO.

It was later shown by Retgers that each of the salts crystallizes separately and does not form compounds from solutions saturated with beryllium sulfate and manganese sulfate.

Investigation of the $BeSO_4$–$MnSO_4$–H_2O system at 25°. Solid phase compositions were determined graphically by the residue method [6] and also on the basis of crystallo-optical analysis. Liquid and solid phases were analyzed for beryllium content alkalimetrically [7], and also gravimetrically as BeO [8]. Manganese was determined by a volumetric procedure, according to Volhard [9]. Solution densities were determined using pycnometers. Based on the data obtained (Tables 1,2), we constructed a solubility isotherm (Fig. 1) and a density isotherm (Fig. 2) for the $BeSO_4-MnSO_4-H_2O$ system at 25°. The isotherms consist of two branches corresponding to crystallization from solution of the solid phases $BeSO_4 \cdot 4H_2O$ and $MnSO_4 \cdot 5H_2O$. Formation of double salts and solid solutions was not observed in the given system under these conditions.

TABLE 1

$BeSO_4-MnSO_4-H_2O$ System at 25°

Expt. No.	Liquid phase composition (wt. %)		"Residue" composition (wt. %)		Bottom phase
	$BeSO_4$	$MnSO_4$	$BeSO_4$	$MnSO_4$	
1	28.7	–	–	–	$BeSO_4 \cdot 4H_2O$
2	25.14	4.84	60.10	–	
	–	–	59.90	–	
3	23.14	10.03	46.27	3.02	
	–	–	45.14	3.30	
4	20.67	15.09	not analyzed *		
5	18.64	18.03	45.82	6.18	
	–	–	46.88	5.64	
6	17.00	21.39	45.10	7.71	
	–	–	45.60	7.35	
7	17.29	21.22	39.18	20.33	$BeSO_4 \cdot 4H_2O$ + + $MnSO_4 \cdot 5H_2O$
	–	–	32.43	21.11	
8	13.66	25.41	6.20	45.00	$MnSO_4 \cdot 5H_2O$
	–	–	6.20	45.50	
9	7.40	30.05	3.10	46.70	
10	5.25	33.00	not analyzed*		
11	–	39.37	–	–	
12	7.48	29.90	5.1	46.13	$MnSO_4 \cdot 4H_2O$
13	14.89	24.44	7.00	47.62	
			6.14	49.70	

* Determined by a crystallo-optical method

TABLE 2

$BeSO_4-MnSO_4-H_2O$ System at 25°
Liquid Phase Densities

Liquid phase composition (mol. %) $MnSO_4$	d^4_{25}
–	1.279
11.80	1.316
23.08	1.358
33.55	1.384
40.20	1.407
46.68	1.430
56.37	1.455
73.97	1.476
100	1.500

In the portion of the system we studied, where the solutions were saturated with manganese sulfate (in the last two tests of Table 1 and in Fig. 1), the bottom phase was a metastable form of manganese sulfate having the composition $MnSO_4 \cdot 4H_2O$.

With regard to the existence of such a hydrate, there are references by a number of authors [10, 11] who

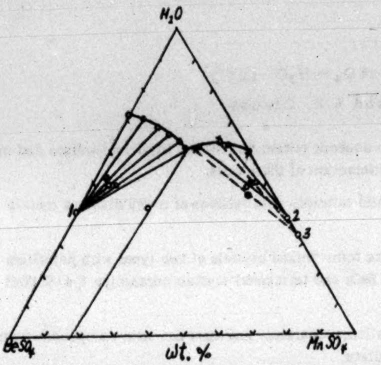

Fig. 1. $BeSO_4-MnSO_4-H_2O$ system at 25°. Solubility isotherms: 1) $BeSO_4\cdot4H_2O$; 2) $MnSO_4\cdot5H_2O$; 3) $MnSO_4\cdot4H_2O$.

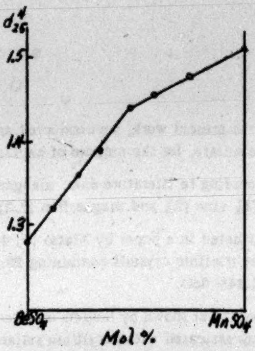

Fig. 2. $BeSO_4-MnSO_4-H_2O$ system at 25°. Liquid phase density isotherm.

were investigating solubility polytherms of manganese sulfate in water.

SUMMARY

1. Solubility and density isotherms for the $BeSO_4-MnSO_4-H_2O$ system at 25° were investigated.

2. It was found that beryllium sulfate and manganese sulfate reduce each other's solubility.

3. It was established that the solid phases in the $BeSO_4-MnSO_4-H_2O$ system at 25° were $BeSO_4\cdot4H_2O$, $MnSO_4\cdot5H_2O$, and the metastable $MnSO_4\cdot4H_2O$.

4. Formation of double salts or solid solutions was not observed in the system.

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DISTRIBUTION OF ISOMORPHIC AND ISODIMORPHIC COMPONENTS BETWEEN SOLID AND LIQUID PHASES IN CRYSTALLIZATION FROM AQUEOUS SOLUTIONS

I. EQUILIBRIUM AT 20° IN SEVERAL SYSTEMS WITH COMPONENTS OF THE COPPERAS TYPE

G. I. Gorshtein and N. I. Silantyeva

The question of laws for equilibrium distribution of isomorphic components between liquid and solid phases in crystallization from aqueous solutions already arose at the time the Van't Hoff theory of solid solution formation was being developed [1].

Roozeboom [2], continuing the classical studies of the Russian scientist Konovalov [3], in studying the equilibrium between liquid and vapor phases in two component systems, developed the classification of three component systems with two isomorphic components (the third component was solvent, usually water).

These authors directed their attention on the important aspect of studying the quantitative laws for equilibrium distribution of isomorphic components between liquid and solid phases. However, in the course of more than 20 years since they did this, there have been only a few separate attempts [3, 4, 5, 6] to solve this question which, moreover, have not had successful results.

Many cases on studies of different systems with isomorphic and isodimorphic components are limited to the obtaining of tables and diagrams which link equilibrium liquid and solid phase compositions without any theoretical discussion. The lack of a guiding theoretical principle promoted inadequate reliability in many experimental investigations of systems with isomorphic components. The first fundamental change of position in this field was connected with the appearance (about 1924) of the classical studies by the Khlopin school [7] (Khlopin, Nikitin, Polesitsky, Ratner, and others) on studying equilibrium distribution of actual isomorphic microcomponents during crystallization of salts from water solutions.

As a result of further investigations, the linear rule for distribution of isomorphic impurities was established. Radioactive substances were used as microcomponents; this facilitated obtaining rapid and also sufficiently accurate results. The Khan school [8] conducted work in this direction.

According to the Khlopin rule, the equilibrium distribution of an isomorphic or isodimorphic microcomponent is characterized by a constant D_{eq} – the ratio of the microcomponent concentration in the solid phase to its concentration in the solute portion of the mother liquor [D_{eq} is usually here called the equilibrium distribution coefficient, but the terms crystallization coefficient (Khlopin) and coefficient of isomorphic mixing (Chirkov) are also employed.

Ratner [9] presented a thermodynamic theory for equilibrium distribution of isomorphic microcomponents between solid and liquid phases.

The most important achievement of this paper was the development of a very rapid, and at the same time reliable, method for attaining equilibrium of specific microcomponents between liquid and solid phases. Studies of the Khlopin school were conducted at very low concentrations of the isomorphic component – of the order of 10^{-12} to 10^{-3} mol.%. In Chirkov's studies [10] on distribution of Br' or I' impurities in crystallizing potassium, sodium, and magnesium chlorides from aqueous solutions, the Khlopin distribution rule was confirmed for microconcentrations to about 1.5% in the solute portion of the mother liquor.

There remains, naturally, the open question on the laws of component distribution during transition from micro- to macroconcentrations, and the question on the general nature of equilibrium distribution curves.

Attempts have been made [14] to express the distribution curves by the formula $y_A = x_A^m$, where x_A is concentration of any component A in solute portion of mother liquor; y_A is concentration of the same component in solid phase; $\underline{m}$ is a constant, characteristic of the given system at a given temperature. In actuality, this empirical formula does not have a general character, because it gives $\frac{dy_A}{dx_A} = 0$ or $\frac{dy_A}{dx_A} = \infty$, for microconcentrations of component A, whereas the value of $\frac{dy_A}{dx_A}$ is equal to D_{eq} for microconcentrations.

Evidently, for ordinary methods of expressing component concentrations in the solid phase and in the solute portion of the mother liquor, the Khlopin linear distribution law may be applicable only for a very restricted narrow portion of the equilibrium curve.

However, the concentration of one component A may be expressed as a ratio to the concentration of the other component B in the same phase, and we may interpret as the equilibrium distribution coefficient of component A, the ratio of these "relative" concentrations for component A in the solid phase and in the mother liquor:

$$D_{eq}\,(A, B) = \frac{y_A}{y_B} \Big/ \frac{x_A}{x_B}$$

Then the D_{eq} (A, B) value, or its reciprocal D_{eq} (B, A), may be constant not only for microconcentrations of one component, but also over a wide interval of macroconcentrations and even for the entire range of component concentrations. Systems for which the D_{eq} value is constant, appear "ideal" at any concentration of components or in definite regions of component concentration corresponding to a concentration interval having a constant D_{eq} value. In the particular case in which the D_{eq} (A, B) value is equal to unity (the equilibrium curve lies along the the diagram diagonal), the system is "congruent".

For ideal systems, the usual distribution diagram curves have hyperbolic shape, expressed analytically as:

$$y_A = \frac{100 D_{eq}\, x_A}{100 - x_A (1 - D_{eq})},$$

where x_A and y_A are concentrations of component A in solute portion of mother liquid and in solid phase; D_{eq} is the equilibrium distribution coefficient value for component A as compared with component B.

Generalizing the meaning of equilibrium distribution coefficient for microconcentrations and for macroconcentrations of the components ensues also from thermodynamic development of the equilibrium distribution question made by Shlezinger and Zorkina [11], Hill, Durham, and Ricci [12], and by Shishkin [13]. Hill and his coworkers studied equilibrium distribution of isomorphic components in several systems with double salts of the alum and schoenite types; however, the experimental data they obtained are in part incompletely reliable, and together with this, conclusions with regard to ideality of the systems under study are not always sufficiently established. The authors do not use the D_{eq} value, but rather its logarithm, which tends to cover the nonuniform scattering of D_{eq} determination results.

Activity formulas obtained for D_{eq} by various authors on a theoretical thermodynamic basis differ from one another, as a rule, only in methods of expressing concentrations and activity coefficients. For systems with ionic crystals, we regard as most suitable the formula in which activity coefficients do not appear for the separate ions in solution, but rather the average activity coefficient of the components—according to Lewis [15].

$$D_{eq}^{v+}\,(A,B) = \left(\frac{L_B}{L_A} \cdot \frac{\gamma_0^{v}\,B^{\pm}}{\gamma_0^{v}\,A^{\pm}}\right) \cdot \frac{\gamma_{\pm A}^{v}}{\gamma_{\pm B}^{v}} \cdot \frac{\gamma_{SB}^{v+}}{\gamma_{SA}^{v+}} \tag{1}$$

Where: L) solubility product of the pure components; [*]
v) total number of ions into which the molecules of each component electrolytically dissociate;
v^+) is the number of non-common ions obtained on dissociating molecules of both components;
$\gamma_{0\pm}$) is the average activity coefficient for each component in pure saturated solution;
$\gamma_{\pm}$) is the average activity coefficient for each component in equilibrium with solid phase in mother liquor containing both components;
γ_S is the activity coefficient for each component in the solid solution; here the standard state ($\gamma_S = 1$) corresponds to taking the component as a pure solid phase.

In formula (1) the product taken in parenthesis has a constant value indpendent of the ratio of component concentrations.

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[*] In the event of isodimorphism, the solubility product corresponds to those modifications of each component which appear in the solid solution.

Thus, deviation of the system from ideality is connected with changes in the ratios:

$$\frac{\gamma_{\pm A}}{\gamma_{\pm A}} \text{ and } \frac{\gamma_{SB}}{\gamma_{SA}}$$

In cases when the non-common ions of isomorphic components have similar radii measurements (which is common). identical types of external electronic shells. and also with components which are not too strongly different in solubility, we may expect that:

$$\frac{\gamma_{\pm A}}{\gamma_{\pm B}} = 1 \text{ and } \frac{\gamma_{SB}}{\gamma_{SA}} \cong 1.$$

Then the system will be approximately ideal for the case of isomorphic components in any ratio, and in the event of isodimorphism — in the region of existence of solid solutions having certain structures. Calculation of the D_{eq} value for individual points connecting compositions of solid and liquid phases, based on experimental data, does not pose particular difficulty.

Things are otherwise with regard to the possibility of determing the D_{eq} value from the thermodynamic formula (1). Even for ideal systems, calculation of D_{eq} by this formula is associated with major complications, in view of the absence of experimental data on activity coefficients for electrolytes in saturated aqueous solutions. It is even more difficult to take account of the system's deviation from ideality in connection with activity coefficients for individual components in the mother solution and solid phases. Together with this, the possiblity of forecasting the degree of entraining specific isomorphic impurities in crystallizing any salt from an aqueous solution has important practical significance. In isomorphism, components less soluble than the salt usually tend to enter the solid phase to a larger degree than more soluble salts, but there may even be exceptions on account of corrections connected with the activity coefficients of the components. In isodimorphism, this criterion generally loses significance — if one does not consider the seldom known solubility of metastable modifications of the components.

The D_{eq} value is more or less dependent on temperature. Character and composition of the solvent may also have areal effect on the D_{eq} value; in certain cases solution pH and addition of complex formers promote changes in activity coefficients of components in solution. One of us [16] has discussed two rules, which enable approximate calculation of D_{eq} values in a number of cases for systems which have not been studied experimentally.

First rule. For isomorphic substances which form a congruent system at the given temperature (third component — solvent). any isomorphic or isodimorphic impurities come down in approximately the same degree during crystallization from solution.

For small deviations from congruence, we may introduce appropriate correction. bearing in mind the fact that the greater the transition of a substance into the solid phase, the less the degree to which any isomorphic or isodimorphic impurity is carried down.

Second rule. If values of the equilibrium distribution coefficients are known for an ideal system containing the isomorphic components A and B and for one containing components B and C. then one may find the D_{eq} value for an ideal system containing components A and C by the formula:

$$D_{eq}\ (A, C) = D_{eq}\ (A, B)\ \ D_{eq}\ (B, C).$$

The second rule can be readily obtained from formula (1); the first rule arises from the similarity of properties of components forming a congruent system.

In our previously published investigation [16] on distribution of impurities during crystallization of inorganic salts, it was confirmed that the Khlopin linear distribution rule was applicable and D_{eq} values were found for various systems with isomorphic and isodimorphic components.

It was also shown there that certain systems with isomorphic and isodimorphic components were ideal over a wide component concentration interval.

In the present contribution, we present results of studying a number of systems with two isomorphic or isodimorphic components which were performed over the entire interval of concentration for both components for the purpose of exploring the laws of equilibrium distribution between solid and liquid phases.

Methods for Studying Equilibrium between Solid and Liquid Phases in Systems with Isomorphic Components

The question of methods for attaining equilibrium between solid and liquid phases in systems with isomorphic or isodimorphic components is associated with special difficulties which are not encountered in study of systems with nonisomorphic components.

The numerous variants of the method of study may be subdivided into two groups: 1) "recrystallization" methods — involving lengthy agitation of crystals of both components with the solution at various starting ratios for the components in the solid and liquid phases, and 2) methods of crystallization from supersaturated solutions under varying conditions of performing the crystallization processes. In the event the former methods are used, equilibrium is attained as a result of a very slow process of recrystallization. Duration of the experiments is large, generally of the order of several weeks, and in a number of cases it is nevertheless difficult to obtain reliable results.

In using methods of crystallization from supersaturated solutions by cooling hot concentrated solutions or by isothermally evaporating, they try to perform the experiment with a very small degree of separation of the substance into the solid phase — with a total degree of crystallization not greater than about 5%. This causes significant prolongation of the experiments.

In using methods of crystallization from supersaturated solution, they do not always consider the important significance of the conditions for performing the crystallization process.

One of us [17] gave a theoretical treatment of the problem of deviation from equilibrium distribution of isomorphic components in relation to the methods and conditions of crystallization from supersaturated solutions. On the basis of this study, it can be shown that a small total degree of crystallization of the substance does not always guarantee a sufficient approximation to the equilibrium state.

The Khlopin school, in studying distribution of isomorphic microcomponents during crystallization of salts from aqueous solutions, developed a remarkably rapid method for attaining equilibrium between solid and liquid phases — a method of relieving supersaturation isothermally with energetic agitation [7]. Equilibrium is usually reached by this method in 4 — 5 hours.

This method for reaching equilibrium was widely used by us for studying systems with macroconcentrations of both isomorphic components.

After performing the crystallization operation, analyses were made for both isomorphic components in the initial solution, the mother liquors, and the crystals separated from the mother liquors. Solid phase composition was calculated using a formula derived on the basis of Shreinemaker's method of residues.

$$C_{SA} = \frac{C_{CA} - \dfrac{C_{MA} - C_{CA}}{C_{CB} - C_{MB}} \cdot (100 - C_{CB})}{1 - \dfrac{C_{MA} - C_{CA}}{C_{CB} - C_{MB}}}$$

where C_{SA} is the concentration of component A in the solid phase (%); C_{MA} and C_{MB} are concentrations of components A and B in the mother liquor (%); C_{CA} and C_{CB} are concentrations of components A and B in the crystals (%).

The D_{eq} (A, B) value is calculated by the formula:

$$D_{eq}\,(A,\,B) = \frac{C_{SA}}{100 - C_{SA}} \cdot \frac{C_{MB}}{C_{MA}}.$$

Equilibrium in the $FeSO_4 - COSO_4 - H_2O$ system at 20°. Both isomorphic components form heptahydrated salts at 20° in the monoclinic system. The concentration of $FeSO_4 \cdot 7H_2O$ in the crystals and mother liquors was determined by titrating with potassium permanganate; concentration of $CoSO_4 \cdot 7H_2O$ was determined by potentiometric titration with potassium ferricyanide.

Experimental results are given in Table 1, in the equilibrium composition diagram (Fig. 1), and in the component distribution diagram (Fig. 2). The system is ideal for the entire concentration interval for each component (from 0 to 100% in the solute portion of the mother liquor). The D_{eq} (Fe, Co) value was 1.20. The D_{eq} (Co, Fe) value was 0.84.

TABLE 1

Experiment number	Analytical results on crystals (%)		Analytical results on mother liquors		% $FeSO_4 \cdot 7H_2O$ In solid phase	% $FeSO_4 \cdot 7H_2O$ In solute portion of mother liquor	Distribution coefficient	
	$CoSO_4 \cdot 7H_2O$	$FeSO_4 \cdot 7H_2O$	$CoSO_4 \cdot 7H_2O$	$FeSO_4 \cdot 7H_2O$			D(Co, Fe)	D(Fe, Co)
1	–	–	48.16	–	0.00	0.00	–	–
2a	82.90	9.59	38.81	3.77	10.43	8.86	0.83	1.20
2b	82.32	9.56	38.80	3.81	10.51	8.94	0.83	1.20
3	71.85	20.81	34.92	8.54	22.65	20.72	0.84	1.19
4a	58.16	34.32	27.68	13.84	37.33	33.33	0.84	1.19
4b	58.22	34.32	27.97	13.59	37.35	32.72	0.81	1.23
5a	55.19	39.43	25.71	15.45	41.85	37.55	0.83	1.20
6a	29.77	65.17	13.89	25.71	68.79	64.92	0.84	1.19
6b	29.79	64.12	14.29	25.89	68.45	64.43	0.83	1.20
7a	17.78	76.93	8.09	29.67	81.32	78.07	0.84	1.19
7b	17.97	78.24	8.00	29.47	81.38	78.64	0.84	1.19
8	–	–	–	37.05	100.00	100.00	–	–

The system may be regarded as approximately congruent because the D_{eq} value does not deviate much from unity and because the distribution curve (Fig. 2) falls almost on the diagonal. The relationship of the $FeSO_4 \cdot 7H_2O$ concentration in the mother liquor $-C_{Fe}-$ to the $CoSO_4 \cdot 7H_2O$ concentration $-C_{Co}-$ is expressed on the equilibrium composition diagram by a straight line whose equation is $\frac{C_{Fe}}{Co_{Fe}} + \frac{C_{Co}}{Co_{Co}} = 1$, where Co_{Fe} and Co_{Co} are solubilities of the pure starting components.

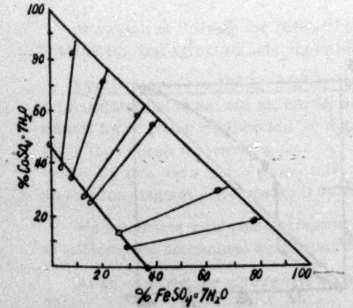

Fig. 1. Equilibrium in $FeSO_4-CoSO_4-H_2O$ system at 20°.

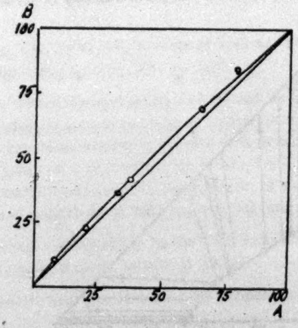

Fig. 2. Distribution curve for components of the $FeSO_4-CoSO_4-H_2O$ system at 20°.

A) % $FeSO_4 \cdot 7H_2O$ in solute portion of mother liquor

B) % $FeSO_4 \cdot 7H_2O$ in solid phase.

Equilibrium in the $FeSO_4$-$NiSO_4$-H_2O system at 20°. Both components crystallize at 20° as heptahydrated salts; however, ferrous sulfate forms crystals in the monoclinic system while nickel sulfate is in the rhombic system. Consequently, both salts are isodimorphic at 20°. The $FeSO_4 \cdot 7H_2O$ concentration was determined in the mother liquors and crystals by titrating with potassium permanganate. The $NiSO_4 \cdot 7H_2O$ concentration was determined by a gravimetric procedure —precipitating with dimethylgloxime after first oxidizing Fe^{++} to Fe^{+++} using hydrogen peroxide.

As can be seen from Table 2 and from the digram (Fig. 3), two solid solution regions are obtained in the system at 20°: one with a rhombic structure of the $NiSO_4 \cdot 7H_2O$ type and one with a monoclinic structure of the $FeSO_4 \cdot 7H_2O$ type. Each of the stated regions is ideal and is characterized by a constant distribution coefficient value. For the $NiSO_4 \cdot 7H_2O$ type solid solution region (the iron salt plays the part of an impurity), the equilibrium distribution coefficient value for $FeSO_4 \cdot 7H_2O$, $\underline{D}_{eq}$ (Fe, Ni), was found to be 0.50; for the $FeSO_4 \cdot 7H_2O$ type solid solution region (the nickel salt plays the part of an impurity), $\underline{D}_{eq}$ (Ni, Fe) was obtained and = 0.41.

Deviation from ideality in either region does not exceed ± 5% relative. The relationship between concentrations of the components in saturated solutions inboth regions is expressed by straight lines (Fig. 3). These two lines intetsect in an invariant point. The equation for the straight line in the region of existence of $FeSO_4 \cdot 7H_2O$ type solid solutions of the monoclinic system is:

$$\frac{\underline{C}_{Fe}}{Co_{Fe}} + \frac{\underline{C}_{Ni}}{Co_{Ni}} = 1,$$

where $\underline{C}_{Fe}$ and $\underline{C}_{Ni}$ are concentrations of $FeSO_4$ and NiSC in the mother liquors, $\underline{Co}_{Fe}$ is the $FeSO_4$ concentration in a saturated ferrous sulfate solution, and $\underline{Cd}_{Ni}$ is the concentration of a saturated solution of a metastable monoclinic nickel sulfate modification. An analogous kind of equation was obtained for the region of existence of the rhombic system $NiSO_4 \cdot 7H_2O$ type solid solutions. By extrapolating the solubility line for the solid solutions until they intersect the coordinate axes, it is possible to obtain approximate solubility values for metastable modifications of both salts, namely ferrous sulfate in the rhombic system and nickel sulfate in the monoclinic system.

Experimental results for the $NiSO_4$-$FeSO_4$-H_2O system at 20° enable confirming, for one particular case, the applicability of the first of two previously stated rules for approximately calculating equilibrium distribution coefficient values for isomorphic impurities. As was shown earlier, the $FeSO_4$-$CoSO_4$-H_2O system could be considered approximately congruent at 20° with a deviation of 15% from congruence (the cobalt salt enters the solid phase to a smaller degree). According to the first rule, the equilibrium distribution coefficient for any isomorphic or isodimorphic impurity in crystallizing ferrous sulfate must amount to about 0.85 of the equilibrium distribution coefficient value for the same impurity in crystallizing cobalt sulfate.

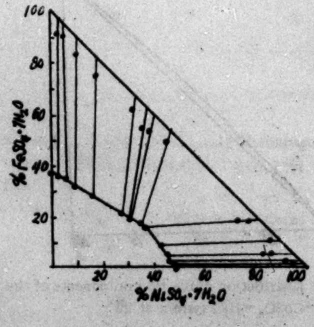

Fig. 3. Equilibrium in the $FeSO_4-NiSO_4-H_2O$ system at 20°.

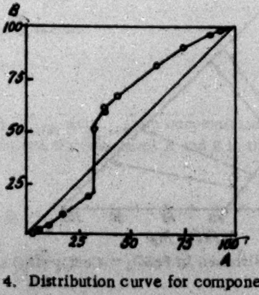

Fig. 4. Distribution curve for components of the $FeSO_4-NiSO_4-H_2O$ system at 20°.
A) % $FeSO_4 \cdot 7H_2O$ in solute portion of mother liquor; B) % $FeSO_4 \cdot 7H_2O$ in solid phase.

In a previously published paper [16], it was found that the D_{eq} value for Ni as an impurity in crystallizing cobalt sulfate at 20° was equal to 0.53. The D_{eq} value for Ni as an impurity in crystallizing ferrous sulfate would then be determined, according to the first rule as $0.53 \cdot 0.85 = 0.45$.

TABLE 2

Test No.	Analytical results (%)					
	Starting solution		Crystals		Mother liquor	
	$FeSO_4\cdot 7H_2O$	$NiSO_4\cdot 7H_2O$	$FeSO_4\cdot 7H_2O$	$NiSO_4\cdot 7H_2O$	$FeSO_4\cdot 7H_2O$	$NiSO_4\cdot 7H_2O$
1	2	3	4	5	6	7
1	–	–	–	–	–	49.20
2a	0.99	52.54	1.20	95.00	1.29	47.85
2b	0.99	52.54	1.27	94.21	1.30	48.10
3a	2.36	51.12	2.32	91.86	2.34	46.48
3b	2.36	51.12	2.41	93.80	2.36	46.66
4a	5.12	51.07	5.45	86.47	5.13	43.82
4b	5.12	51.07	5.51	89.96	5.13	43.28
5a	4.84	53.14	5.17	85.03	4.87	44.96
5b	4.84	53.14	5.07	82.94	4.92	45.24
6a	9.23	47.20	10.03	85.91	9.08	42.69
6b	9.23	47.20	9.93	85.31	9.19	42.79
7a	16.33	43.44	18.34	77.55	16.27	36.40
7b	16.33	43.44	18.29	72.83	16.19	36.33
8a	20.30	35.92	49.28	44.70	16.75	34.69
8b	20.30	35.92	49.54	45.31	16.83	34.92
9a	22.68	31.00	52.29	39.49	18.61	29.72
9b	22.68	31.00	54.18	36.05	18.20	30.42
10a	32.89	29.05	61.38	32.39	21.18	27.23
10b	32.89	29.05	61.43	32.62	21.30	27.26
11a	35.69	16.67	75.01	18.42	27.70	16.41
11b	35.69	16.67	75.08	18.75	27.60	16.31
12a	40.49	9.18	82.58	10.09	31.78	9.24
12b	40.49	9.18	83.44	10.02	31.92	9.09
13a	42.09	6.82	89.59	4.99	34.94	4.50
13b	42.09	6.82	88.58	5.08	35.04	4.47
14a	44.40	2.45	91.05	2.75	36.40	2.46
14b	44.40	2.45	91.21	2.76	36.22	2.47
15	–	–	–	–	37.05	–

As a result of studying the $NiSO_4-FeSO_4-H_2O$ system, a D_{eq} (Ni, $FeSO_4\cdot 7H_2O$) value of 0.41 was experimentally obtained; this agrees sufficiently satisfactorily with results from calculation by the first rule.

Equilibrium in the $NiSO_4-MgSO_4-H_2O$ system at 20°. This system was studied by Benrath and Neumann [18] at temperature of 0, 35, 40, 45, 60, 75, 80, and 100°. In their studies, these authors used a "recrystallization" method for attaining equilibrium; in this, crystals and solution were stirred for about 4 weeks with periodic crushing of the crystals for renewing their surfaces. The authors only give tables of composition for the crystals and mother liquors; they do not present solid phase compositions, an equilibrium composition diagram, or a component distribution diagram. This makes it difficult to judge the degree of reliability of the experimental results.

We calculated solid phase compositions from the work of Benrath and Neumann by the Shreinemaker method of residues, and determined distribution coefficient values of the components at individual points.

As an example, we give results of our calculations on the Benrath and Neumann data for temperatures of 0° and 35°.

At a temperature of 0°, both salts are isomorphic (heptahydrated rhombic system).

As can be seen from Table 3, the equilibrium distribution coefficient value for either component, for example the magnesium salt, $-\underline{D}_{eq}$ (Mg, Ni) $-$varies in a non-uniform manner from 0.42 to 1. This phenomenon is observed even to a greater extent at 35°, as shown in Table 4 in which the results of calculating at this temperature are given.

Thus, despite the long duration of the Benrath and Neumann experiments, their results should be regarded as of low reliability. We investigated this system only at the single temperature of 20° (the components are isomorphic

α total	% $FeSO_4 \cdot 7H_2O$ in solid phase	% $FeSO_4 \cdot 7H_2O$ in solute portion of mother liquor	Distribution coefficient D $D_{Fe, Ni}$	$D_{Ni, Fe}$	Remarks
8	9	10	11	12	
–	0.00	0.00	–		Solid solutions with rhombic structure of the $NiSO_4 \cdot 7H_2O$ type.
0.17	1.20	2.62	0.45		
0.16	1.27	2.63	0.48		
0.17	2.32	4.79	0.47		
0.16	2.41	4.81	0.49		
0.25	5.51	10.49	0.50		
0.27	5.54	10.60	0.49		
0.28	5.25	9.75	0.51		
0.27	5.11	9.80	0.49		
0.17	10.12	17.54	0.53		
0.16	10.00	17.68	0.52		
0.26	18.54	30.88	0.51		
0.27	18.80	30.84	0.52		
		Average . . .	0.50		
0.17	51.59	32.56		0.45	Solid solutions with monoclinic structure of the $FeSO_4 \cdot 7H_2O$ type.
0,16	53.45	32.52		0.42	
0.19	58.75	38.50		0.44	
0.18	61.26	37.43		0.38	
0.42	66.91	43.75		0.38	
0.42	66.69	43.86		0.39	
0.28	81.31	62.79		0.39	
0.29	80.95	62.85		0.40	
0.29	89.79	77.47		0.39	
0.29	89.86	77.83		0.40	
0.32	94.96	88.59		0.41	
0.31	94.85	90.68		0.43	
0.28	97.81	93.66		0.42	
0.28	97.21	93.57		0.42	
–	100.00	100.00	Average. .	0.41	

TABLE 3

Mol. % $MgSO_4$		D_{eq} (Mg, Ni)	D_{av} (Mg, Ni)
In solute portion of mother liquor	In solid phase		
91.8	89.5	0.76	
94.1	77.6	0.65	
75.4	69.2	0.73	
59.2	59.2	1.00	0.69
50.7	41.0	0.68	
43.0	28.0	0.83	
31.8	12.5	0.47	
21.0	9.0	0.42	

at this temperature); one of our purposes was to investigate the possibility of obtaining sufficiently reliable results by using the rapid Khlopin method for attaining equilibrium.

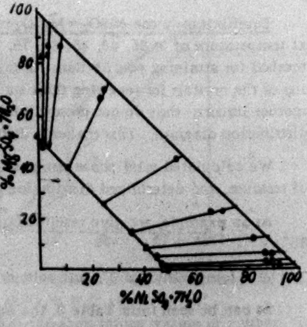

Fig. 5. Equilibrium in the $NiSO_4 - MgSO_4 - H_2O$ system at 20°.

The mother liquors and crystals were analyzed in the following manner. The $NiSO_4 \cdot 7H_2O$ content was determined by electrolyzing nickel from a solution containing

TABLE 4

Mol. % $MgSO_4$		D_{eq} (Mg. Ni)	D_{av} (Mg. Ni)
In solute portion of mother liquor	In solid phase		
97.7	83.0	0.11	0.62
94.1	93.5	0.9	
94.1	97.5	0.44	
80.4	75.5	0.76	
72.8	76.0	1.19	
64.0	56.0	0.72	
55.0	47.0	0.73	
47.0	36.7	0.65	
36.2	27.0	0.57	
26.2	14.2	0.47	
24.3	14.5	0.53	
22.3	13.5	0.56	
20.2	11.7	0.52	
17.7	11.0	0.58	

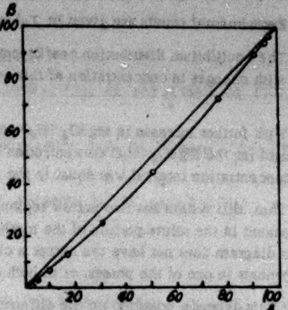

Fig. 6. Distribution curve for components in the $NiSO_4-MgSO_4-H_2O$ system at 20°. A) % $MgSO_4\cdot7H_2O$ in solute portion of mother liquor; B) % $MgSO_4\cdot7H_2O$ in solid phase

TABLE 5

Test No	Analytical results (%)						α total	% $MgSO_4\cdot7H_2O$		Distribution coefficient (D) $D_{Mg, Ni}$
	Starting solution		Crystals		Mother liquor			in solid phase	in solute portion of mother liquor	
	$MgSO_4\cdot7H_2O$	$NiSO_4\cdot7H_2O$	$MgSO_4\cdot7H_2O$	$NiSO_4\cdot7H_2O$	$MgSO_4\cdot7H_2O$	$NiSO_4\cdot7H_2O$				
1	–	–	–	–	–	49.20	–	0.00	0.00	–
2a	1.22	48.54	1.53	91.38	1.20	47.60	0.32	1.59	2.50	0.64
2b	1.22	48.54	1.61	92.09	1.21	48.54	0.29	1.67	2.47	0.68
3a	2.43	51.92	3.01	88.25	2.31	47.10	0.18	3.16	2.55	0.66
3b	2.43	51.92	3.06	89.03	2.29	46.83	0.19	3.02	2.50	0.64
4a	5.09	56.62	6.37	87.27	4.62	45.02	0.39	6.62	9.28	0.69
4b	5.09	56.62	6.19	89.27	4.65	44.87	0.39	6.34	9.39	0.65
5a	11.21	50.58	12.27	81.82	8.60	40.92	0.39	12.88	17.38	0.70
5b	11.21	50.58	12.25	81.61	8.68	41.37	0.38	12.76	17.18	0.70
6a	–	–	23.07	69.93	15.44	35.49	–	24.35	30.31	0.74
6b	–	–	21.71	66.05	15.37	35.21	–	23.81	30.37	0.72
7a	–	–	43.43	52.99	26.27	24.89	–	44.78	51.31	0.77
7b	–	–	43.24	52.81	26.38	25.20	–	44.74	51.22	0.77
8a	45.27	12.72	67.44	24.31	39.85	11.17	0.25	73.01	78.10	0.76
8b	45.27	12.72	70.27	24.57	39.85	11.15	0.25	73.85	78.10	0.79
9a	53.61	4.51	86.68	8.95	48.59	4.11	0.20	90.56	92.21	0.81
9b	53.61	4.51	85.97	8.79	48.72	4.08	0.20	90.62	92.29	0.80
10a	–	–	85.52	4.08	47.70	1.94	–	95.35	96.00	0.83
10b	–	–	83.92	4.15	47.55	1.97	–	95.18	96.00	0.81
11	–	–	83.40	2.31	50.17	1.19	–	97.22	97.70	0.83
12	–	–	–	–	51.37	–	–	100.00	100.00	–

excess ammonia with added ammonium sulfate. Electrolysis was performed at a voltage of 16 V and with a current strength of about 3 A. Platinum gauze was used for the electrodes. The electrolyte was agitated using an electromagnetic stirrer. Duration of electrolysis amounted to 40-60 minutes. The $MgSO_4\cdot7H_2O$ content was determined in the solutions after electrolysis by precipitating twice with diammonium phosphate with subsequent weighing as $MgNH_4PO_4 \cdot 6H_2O$ according to the Vasilyev and Sinkovskaya method [19].

Experimental results are given in Table 5 and in Figures 5 and 6.

The equilibrium distribution coefficient value for $MgSO_4 \cdot 7H_2O$ remained constant at a level which averaged 0.65 with changes in concentration of this component in the solute portion of the mother liquor from zero to about 10%.

With further increase in $MgSO_4 \cdot 7H_2O$ concentration, the D_{eq} (Mg, Ni) value smoothly rose to 0.81, which was held for the $MgSO_4 \cdot 7H_2O$ concentration interval from 90 to 100% [the corresponding D_{eq} (Ni, Mg) value for this concentration interval was equal to the reciprocal, 1.23].

Thus, this system has two narrow regions of "ideality" corresponding to a concentration up to 10% of each component in the solute portion of the mother liquor. Deviation from ideality in the middle portion of the equilibrium diagram does not have too abrupt a character and is caused by differences in activity coefficients for both components in one of the phases, or in both of the phases at the same time.

This depends, possibly, on the difference in the polarization properties of Mg^{++} and Ni^{++} ions in connection with the structure of their external electronic shells. The relation between concentrations of both components in the mother liquors is expressed by straight lines on the equilibrium composition diagram. The results we obtained from studying the $NiSO_4-MgSO_4-H_2O$ system show that the rapid Khlopin method for attaining equilibrium which was used by us was fully reliable, as contrasted with the method used by Benrath and Neumann.

SUMMARY

1. Equilibrium distribution of isomorphic and isodimorphic components was studied in the $FeSO_4-CoSO_4-H_2O$, $NiSO_4-FeSO_4-H_2O$, and $NiSO_4-MgSO_4-H_2O$ systems at 20°; we widely used (for the first time for study of systems at macroconcentrations of isomorphic components) the rapid method for attaining equilibrium developed by Khlopin's school for microconcentrations of one isomorphic component.

2. It was found that the $FeSO_4-CoSO_4-H_2O$ system at 20° was ideal. The D_{eq} (Fe, Co) value was found to equal 1.20; the reciprocal, D_{eq} (Co, Fe) was equal to 0.84.

3. It was found that there were two regions for existence of solid solutions of different structure in the $NiSO_4-FeSO_4-H_2O$ system with isodimorphic components; in each of these regions the system was ideal. The D_{eq} (Ni, Fe) value in the region of existence of the monoclinic system ferrous sulfate type solid solution (nickel salt — impurity) was found to equal 0.41; the D_{eq} (Fe, Ni) value for the region of existence of the rhombic system nickel sulfate type solid solution (iron salt — impurity) was found to equal 0.50.

4. It was found that the $NiSO_4-MgSO_4-H_2O$ system at 20° was ideal only in limited concentration intervals at the ends of the equilibrium composition diagram. Deviation from ideality in the middle portion of the diagram did not have an abrupt character. The equilibrium distribution coefficient value for Mg as an impurity in crystallizing nickel sulfate was found at 20° to be 0.65; the equilibrium distribution coefficient value for Ni as an impurity in crystallizing magnesium sulfate was found to be 1.23.

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* See Consultants Bureau English Translation, p. 1025.

COPPER COMPLEXES WITH DIMETHYLGLYOXIME

A. K. Babko and M. V. Korotun

A complex compound of copper and dimethylglyoxime, as well as with other dioximes, was first separated by L. A. Chugaev [1] in 1905; he showed that this compound was analogous to nickel dimethylglyoxime in some of its properties and that its composition could be expressed by the formula $Cu(HDm)_2$, where HDm^- is a singly charged dimethylglyoxime anion. The compound $Cu(HDm)_2$ was also investigated by V. M. Peshkova [2].

The properties of $Cu(HDm)_2$ have been only slightly studied although knowledge of the properties of this compound, as the first of a large class of internal complex compounds—the dioximes—has significance for the chemistry of complex compounds as well as for analytical chemistry.

Study of the equilibrium between copper and dimethylglyoxime in solution, as performed by us using various methods, shows that the copper-dimethylglyoxime system is rather complicated. Several complex compounds which differ in composition, stability, and optical properties are formed in solution depending on conditions.

Solubility of $Cu(HDm)_2$ in water and in the presence of common ions. The initial $Cu(HDm)_2$ preparation was obtained from copper sulfate and the disodium salt of dimethylglyoxime, taken in a 1:2 ratio. For this, 0.1 mole of the copper salt, dissolved in 250 ml water, was added in small portions to a solution of disodium dimethylglyoxime (0.2 mole dimethylglyoxime and 0.4 mole NaOH in 200 ml water). In these conditions, i.e., in alkaline media, crystalline copper dimethylglyoxime does not separate, in contrast to nickel dimethylglyoxime, but the solution develops a brown color. By neutralizing the alkali using dilute acid, crystals of $Cu(HDm)_2$ separate from solution, with a maximum yield on introducing 0.2 g-equivalents of acid.

Analysis of the air-dried precipitate was conducted in the following manner. The quantity of copper was determined by electrolysis after first decomposing the organic portion using ammonium persulfate in presence of sulfuric acid. Dimethylglyoxime held in the $Cu(HDm)_2$ was precipitated by an excess of a nickel salt as $Ni(HDm)_2$ at a pH of 5. The $Ni(HDm)_2$ precipitate was first washed with buffer solution and then with water. The analytical results presented below indicate adequate purity for the preparation:

Found %Cu 21.58; theoretical 21.54; HDm^- 78.4; theoretical 78.36.

In its free state, the $Cu(HDm)_2$ compound is a black crystalline substance soluble in water, alcohol, acetone, and in other solvents forming reddish-brown solutions. It was first established by its copper content that the water solution became saturated after continuous agitation for a period of 1.5–2 hours. After saturation the liquid was separated from the solid phase using a pipette with a filtering layer. Copper and dimethylglyoxime content of the water solution were determined by methods described above. Solubility found from copper concentration in the filtrate corresponded to solubility as determined from dimethylglyoxime content and was equal to $6 \cdot 10^{-3}$ mole/liter (at 22°).

Solubility values presented do not agree with literature data. Thus, according to data of V. M. Peshkova [2], the solubility of $Cu(HDm)_2$ in water at 20° was 1.12% which corresponds to $3.9 \cdot 10^{-2}$ mole/liter. We cannot explain the reason for this large discrepancy (almost 6.5 fold) because V. M. Peshkova did not report methods for determining solubility.

According to conclusions from the solubility product principle, if new chemical compounds do not form on introducing excess copper ions, we should anticipate decreased solubility of the $Cu(HDm)_2$ precipitate. However, the experiments, a portion of which are presented in Table 1, indicate the complete reverse. Copper sulfate solutions with accurately known concentrations and with a pH not greater than 4 were saturated with copper dimethylglyoxime for a period of 2 hours, after which the total amount of copper in the filtrate was determined. Solubility was calculated from the difference between total and initial copper concentrations.

Table 1

$Cu(HDm)_2$ Solubility in Copper Sulfate Solutions.

Initial copper salt concentration (mole/liter), $C \cdot 10^3$	Total (found) copper salt concentration (mole/liter), $C \cdot 10^3$	$Cu(HDm)_2$ solubility (mole/liter), $C \cdot 10^3$
5.0	13.5	8.5
10.0	18.8	8.8
20.0	30.0	10.0
50.0	62.8	12.8
100.0	114.0	14.0
200.0	218.0	18.0

By comparing data of Columns 1 and 3 in Table 1, it can be seen that solubility of $Cu(HDm)_2$ significantly increases on increasing the concentration of introduced copper salt.

One reason for the precipitate's properties deviating from normal is reaction of the solid phase with copper anions to form ions of the type $PbCl^+$, PbI^+, HgI^+, and so on. By analogy, we may assume that the solubility of $Cu(HDm)_2$ in copper salts is connected with the reaction:

$$Cu(HDm)_2 + Cu^{++} = 2CuHDm^+. \qquad (1)$$

The complex cation $CuHDm^+$. **The assumption presented above with regard to formation of the complex cation $CuHDm^+$ (with excess copper ion) was checked by two methods. Preliminary experiments showed that the optical density of a $Cu(HDm)_2$ solution was changed by introducing either an excess of dimethylglyoxime or an excess of copper ion.** This change in optical density can be explained by a change in dissociation of the complex in presence of an excess of one of its reactant components:

$$Cu(HDm)_2 = Cu^{++} + 2HDm^- \qquad (2)$$

According to equation (2), introducing excess dimethylglyoxime should have considerably more effect than adding excess Cu^{++} ion. Actually, the exact opposite was observed. We placed 5 ml portions of saturated $Cu(HDm)_2$ solution in a series of flasks together with 25 ml pH 5 buffer solution (a mixture of sodium acetate and hydrochloric acid) after which increasing quantities of copper sulfate were added to one set of the flasks, and similarly increasing quantities of dimethylglyoxime added to the other. Each solution was brought to a volume of 50 ml and its optical density measured with a 5 cm layer thickness at a 460 mμ wave length (in this spectral region, copper sulfate solution absorbs almost none of the light) (Fig. 2). Measurement results are given in Fig. 1. Quantity (milliliters) of 0.1 molar dimethylglyoxime solution added (curve 1) or copper solution (curve 2) is plotted along the abscissas, and optical density (D) along the ordinate axis.

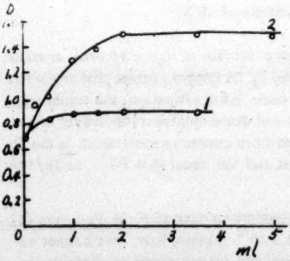

Fig. 1. Change in optical density of $Cu(HDm)_2$ solution with increasing concentration of both ions.

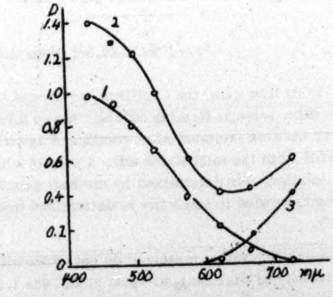

Fig. 2. Absorption spectra of: (1) 0.0006 molar $Cu(HDm)_2$ solution, (2) 0.0006 M $Cu(HDm)_2$ solution in presence of 0.01 mole $CuSO_4$, and (3) 0.01 M $CuSO_4$ solution.

As can be seen from data of Fig. 1, dimethylglyoxime addition has little effect on optical density of the initial $Cu(HDm)_2$ solution; on the contrary, addition of copper salt increases the light absorption of the initial solution by almost 1.5 fold. Consequently, in presence of excess copper ion, no change occurs in dissociation equilibrium but rather a chemical reaction takes place to from a new compound (equation 1).

Formation of a complex cation in this condition was also confirmed by observing motion of the colored complex during electrolysis. For these experiments, we used a U-shaped tube with stopcocks. The lower portion of the tube was filled with copper sulfate solution previously saturated with copper dimethylglyoxime, and a copper sulfate solution of the same concentration (side liquid) was placed in the upper portion. The vessel was connected to a direct current source. In a one hour period, the colored layer noticeably moved toward the cathode.

We also studied complex-formation reactions between copper and dimethylglyoxime in solution by methods of physico-chemical analysis. Optical density was taken as a system property. It should, however, be noted that using physico-chemical methods of analysis is somewhat difficult in the given case because the absorption spectra of both compounds — $Cu(HDm)_2$ and the complex formed with excess copper ion — are rather close (Fig. 2).

Both compounds absorb light rather stronly in the short-wave portion of the spectrum and the difference in their optical properties is of low reliability. In the long-wave region, light absorption for $Cu(HDm)_2$ is very small, whereas that for the complex formed with excess copper salt is significantly greater; consequently, in this spectrum region, the difference between them should be more clearly expressed. However, copper ions show strong light absorption in the long-wave portion of the spectrum.

Measurements of optical density were also performed in the short-wave and central portions of the spectrum. Results are given below on studying optical properties of an equimolar mixture [3] of copper sulfate and the disodium salt of dimethylglyoxime in a solution buffered at pH 4.5 and constant total volume: 0.1 M solutions were mixed in various ratios so that the toal concentration of components (moles/liter) would remain constant. The copper salt concentration decreased in the following manner: $2.4 \cdot 10^{-3}$, $2.2 \cdot 10^{-3}$, $2.0 \cdot 10^{-3}$, and so on. Dimethylglyoxime concentration increased in the same order. Buffer mixture (sodium acetate and hydrochloric acid) was added in the amount of 25 ml per 100 ml total volume, after first neutralizing the disodium salt of dimethylglyoxime with acid. The composition — optical density curves, plotted for comparison in several portions of the spectrum, have the form shown in Fig. 3.

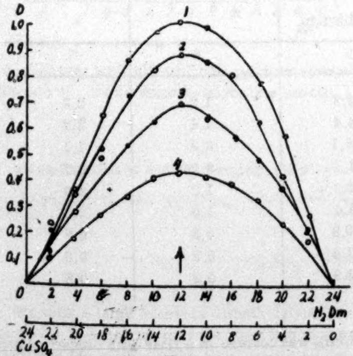

Fig. 3. Composition — optical density curves for the $CuSO_4$ — H_2Dm system at pH 4.5, layer thickness 5 cm. Wave length (λ) (mμ): 1) 436; 2) 495; 3) 533, 4) 574.

At pH 4.5, maximum light absorption was observed in solutions having components in a 1:1 ratio for all portions of the spectrum. On transition to less acid solutions, the maximum shifts to solutions with larger dimethylglyoxime content. Thus for example at pH 5.5 — 6 the maximum is observed for a mixture with a 5:7 compostion (these data are not presented), and at pH 7 — 8 with a 1:2 ratio (Fig. 7). Thus, formation of two compounds in equilibrium with each other takes place in the mentioned conditions. The simpler complex group $CuHDm^+$, forms in low concentrations of the coordination ion (in acid media), With increasing pH, concentration of the free anion HDm^-, from the reagent increases and the compound, $Cu(HDm)_2$, becomes the domdominant form in solution. As was shown above, formation of $CuHDm^+$ is also promoted by introducing excess Cu^{++} ions.

Determining the dissociation constant of $CuHDm^+$ complex by equilibrium with precipitated $Ni(HDm)_2$. Solid $Ni(HDm)_2$ significantly dissolves in presence of a copper salt, although by itself it appears to be one of the most difficultly soluble precipitates. Equilibrium may be attained in a 14 — 16 hour period of continued agitation of the solution. Preliminary experiments also showed that $Ni(HDm)_2$ solubility in copper salt solutions of constant concentration remained approximately the same over wide pH limits. Consequently, in studying the character of the equilibrium, it was sufficient to follow $Ni(HDm)_2$ solubility as a function of copper salt concentration. The $Ni(HDm)_2$ — Cu^{++} system was studied by us only in media having pH below 5, because formation of basic salts was possible at smaller acidities.

In weakly acid media, dissolving may depend on one of the two reactions:

$$Ni(HDm)_2 + Cu^{++} = Cu(HDm)_2 + Ni^{++}, \qquad (3)$$

$$Ni(HDm)_2 + 2Cu^{++} = 2CuHDm + Ni^{++}. \qquad (4)$$

In connection with the data presented above, however, one should expect that in presence of excess free copper ions equilbrium (4) should have the greater significance (compare column 5 in Table 2). In this case, the principle for determining dissociation constants for the CuHDm$^+$ complex numerically characterizing the bond energy between the central Cu^{++} atom and the coordinating HDm$^-$ anions, consists in experimentally determining the equilibrium constant for reaction (4):

$$K_{eq} = \frac{[CuHDm^+]^2\,[Ni^{++}]}{[Cu^{++}]^2} = \frac{SP_{Ni(HDm)_2}}{K^2_{CuHDm^+}}. \qquad (5)$$

where $SP_{Ni(HDm)_2}$ is the solubility product for nickel dimethylglyoxime and K_{CuHDm^+} is the dissociation constant for the CuHDm$^+$ complex.

TABLE 2

Solubility of Precipitated Ni(HDm)$_2$ in Copper Sulfate Solutions at pH 4.5.

Experiment number	Concentration (g-ions/liter) C·10^4				$K_3 \cdot \cdot 10^4$	$K_4 \cdot \cdot 10^5$
	Initial [Cu^{++}]	[Ni^{++}] found in filtrate	[CuHDm$^+$]	[Cu^{++}] equilibrium.		
1	2	3	4	5	6	7
1	800	30.3	60.7	739.3	1.2	2.0
2	500	22.8	45.6	454.4	1.1	2.2
3	100	6.0	11.9	88.1	0.4	1.1
4	80	4.4	8.9	71.1	0.26	0.7
5	800	30.3	60.7	739.3	1.2	2.0
6	500	21.8	43.6	456.4	1.0	2.0
7	100	5.4	10.7	89.3	0.3	0.8
8	80	4.3	8.6	71.4	0.2	0.6
9	50	3.3	6.7	43.3	0.2	0.8

The working conditions were as follows. Crystalline Ni(HDm)$_2$ was covered in a flask with copper sulfate solution of known concentration and with buffer mixture having pH 4.5. The flask contents were continually shaken until saturation. Liquid was removed from the residue using a pipette with a filtering layer. Nickel content of the liquid was determined by precipitation with excess dimethylglyoxime with subsequent recrystallization. The CuHDm$^+$, concentration, forming as a result of reaction, was taken equal to double the nickel concentration, based on equation (4). Equilibrium Cu^{++} ion concentration was found by the difference between initial salt concentration and copper present in the CuHDm$^+$. For approximate calculation of equilibrium constants it was assumed that copper sulfate dissociated completely in solution; moreover, we did not consider the effect of buffer mixture anions and other factors having second - order significance. Data of these experiments are presented in Table 2.

Equilibrium constant values for equation (4), calculated from the principle presented, are given in column 7 of Table 2; equilibrium constants calculated assuming that the reaction follows equation (3) are given in column 6. By comparing the data of columns 6 and 7, it can be seen that K_4 changes less than K_3 with change in the copper ion concentration. This confirms correctness of equation selection. Average K_{eq} value for equation (4) was equal to $1 \cdot 10^{-5}$; $SP_{Ni(HDm)_2}$ is $2.2 \cdot 10^{-25}$ [4]. Setting these values into equation (5), we obtain:

$$K_{CuHDm^+} \quad \sqrt{\frac{2.2 \cdot 10^{-25}}{1 \cdot 10^{-5}}} = 1.5 \cdot 10^{-10}$$

The order of magnitude for the dissociation constant is confirmed by optical investigation data.

Dissociation constant for $CuHDm^+$ complex from studies on optical density as dependent on solution pH. Copper complex formation with dimethylglyoxime, similar to other complex compounds of metals with weakly acid anions, depends strongly on acidity of the medium. In Fig. 4, is presented a curve for change in optical density of a solution containing $5 \cdot 10^{-4}$ mole/liter $CuSO_4$ and an 8-fold excess of dimethylglyoxime with increasing pH.

Light absorption sharply increases over pH limits from 2.8 to 4.5 and then remains constant for pH from 4.5 to 9. With further pH increase, absorption again increases. A curve of this shape is characteristic of stepwise complex formation. The second stage is limited by the region in which alkali decomposes the complex (discussed in detail below).

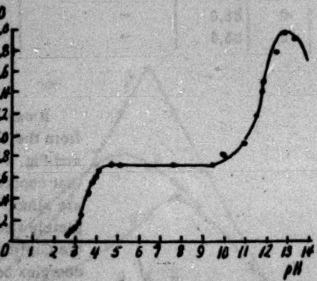

Fig. 4. Change, with pH, of $CuSO_4$ solution optical density in presence of 8-fold dimethylglyoxime excess.

Abrupt increase in the optical density curve between pH 2.8 to 4.5 may be attributed to formation of either complex: $CuHDm^+$ or $Cu(HDm)_2$. If the reaction taking place here may be expressed by the scheme:

$$Cu^{++} + nH_2Dm = Cu(HDm)_n + nH^+, \qquad (6)$$

then, from the equation for equilibrium constant:

$$K_{eq} = \frac{[Cu(HDm)_n]\ [H^+]^n}{[Cu^{++}]\ [H_2Dm]^n} \qquad (7)$$

after taking logarithms and rearranging, we obtain the equation:

$$-n \log [H^+] = -\log K_{eq} \cdot [H_2Dm]^n + \log \frac{[Cu(HDm)_n]}{[Cu^{++}]}. \qquad (8)$$

We took a large excess of dimethylglyoxime in a series of solutions so that the $[H_2Dm]$ value could be taken as constant. The first term of the right side of the equation then likewise becomes constant (A), and the relationship between the variables can be expressed by the linear equation:

$$n\ pH = A + \log \frac{[Cu(HDm)n]}{[Cu^{++}]} \qquad (9)$$

where n — is the slope (tan α), numerically equal to the quantity of HDm^- coordination ions. Thus, if solution pH is known, the problem reduces to experimentally determining $Cu(HDm)_n$ complex concentration. In Table 3 optical densities are given for a solution containing $5 \cdot 10^{-4}$ moles/liter $CuSO_4$ and $40 \cdot 10^{-4}$ moles/liter dimethylglyoxime at various pH.

TABLE 3

Optical Density of a 5'10^{-4} Molar $CuSO_4$ Solution (in Presence of 8-fold Excess Dimethylgloxime) as Dependent on pH. Absorption Layer Thickness 5 cm.

Experiment Number	$[H^+]$ (g ions/liter) $C \cdot 10^4$	pH	Optical density D at λ = 436 m μ	Concentration (moles/liter) $C \cdot 10^4$ $[Cu(HDm)_n]$	$[Cu^{++}]$	$[H_2Dm]$	$\log \frac{Cu(HDm)_n}{[Cu^+]} + 1$	$K_{eq} \cdot 10^5$
1	2	3	4	5	6	7	8	9
1	25	2.6	0.07	0.5	4.5	39.5	0.0457	0.7
2	19.9	2.7	0.09	0.6	4.4	39.4	0.1347	0.7
3	7.9	3.1	0.17	1.2	3.8	38.8	0.4994	0.6
4	5.0	3.3	0.25	1.7	3.3	38.3	0.7119	0.7
5	3.2	3.5	0.36	2.5	2.5	37.5	1.0000	0.9
6	2.5	3.6	0.46	3.2	1.8	36.8	1.2499	1.2
7	1.6	3.8	0.55	3.8	1.2	36.2	1.5006	1.4
8	1.0	4.0	0.60	4.2	0.8	35.8	1.7202	1.5
9	0.6	4.2	0.67	4.7	0.3	35.3	–	–
10	0.3	4.5	0.72	5.0	0	35.0	–	–
11	0.06	5.2	0.72	5.0	0	35.0	–	–

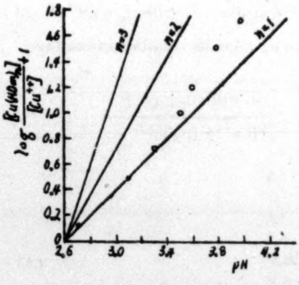

Fig. 5. Change in log $\frac{[Cu(HDm)n]}{[Cu^{++}]}$ as dependent on pH.

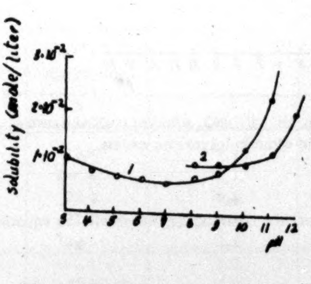

Fig. 6. $Cu(HDm)_2$ solubility in buffered solutions. Curve 1) solubility in acetate solution; Curve 2) solubility in borate solution.

It can be seen from the Table 3 and Fig. 4 data that copper ions are almost completely tied up in the $Cu(HDm)_n$ complex beginning with pH 4.8. The optical density of such a solution was equal to 0.72. Consequently, we may calculate the $Cu(HDm)_2$ concentration in other solutions from their optical density. The equilibrium Cu^{++} ion concentration is equal to the difference between the initial total Cu^{++} concentration and the copper tied up in the complex. Fig. 5 was plotted based on the data of Table 3 and reflects equation (9), i.e., the dependence of log $\frac{[Cu(HDm)_n]}{[Cu^{++}]}$ (ordinate axis) to pH (abscissas axis); both variables are plotted to the same scale here. The straight lines show relationships calculated assuming that n = 1, n = 2, and n = 3; the points correspond to the experimental results.

Over pH limits from 2.6 to 3.6, experimental data are close to the line with n = 1; it follows from this that the number of coordinating HDm^- ions is likewise equal to unity, i.e., in acid media the complex $CuHDm^+$ forms to the largest extent, according to the equation:

$$Cu^{++} + H_2Dm = CuHDm^{+} + H^{+}. \tag{10}$$

With further increase in pH the slope increases, evidently in consequence of forming significant quantities of the complex $Cu(HDm)_2$.

Data of Table 5 were also used for calculating dissociation constants for the $CuHDm^{+}$ complex by a relationship derived from equation (10):

$$K_{eq} = \frac{[CuHDm^{+}][H^{+}]}{[Cu^{++}][H_2Dm]} = \frac{K_{H_2Dm}}{K_{CuHDm^{+}}} \tag{11}$$

from which:

$$K_{CuHDm^{+}} = \frac{K_{H_2Dm}}{K_{eq}} \tag{12}$$

where K_{H_2Dm} is the first dissociation constant for dimethylglyoxime, numerically equal to $8 \cdot 10^{-12}$ [5]. The equilibrium constant, based on a large number of experiments, only a portion of which are presented in Table 5,* was approximately equal to $1 \cdot 10^{-1}$. Consequently $K_{CuHdm^{+}} = 0.8 \cdot 10^{-10}$; this is close to the numerical value for the constant as found by entirely different procedures, namely by equilibrium with precipitated $Ni(HDm)_2$ (see above).

Copper complexes with dimethylglyoxime in alkaline media. The $Cu(Hdm)_2$ complex is soluble in alkalies — NaOH and KOH — with formation of greenish-brown solutions. On neutralizing the alkaline solutions, $Cu(HDm)_2$ again crystallizes. Increase in solubility with increasing solution pH is shown in Fig. 6.

The solubility changes slightly over rather wide pH limits (from 4 to 9). At pH above 9 it significantly increases. It is characteristic that the solubility curve increase is located at the very same pH limits at which optical density increases (Fig. 4).

$Cu(HDm)_2$ was observed to be similar to the dioximes $Pd(HDm)_2$ and $Pt(HDm)_2$, both of which likewise are readily soluble in alkalies. L.A. Chugaev, [1] claimed that reaction with alkalies indicated acid properties in the dioximes, implying by this, evidently, the tendency to replace two hydrogen atoms remaining in the oxime groups. To the present time, however, it has not been possible to determine the composition of products formed in alkali and to explain the reaction chemistry. In connection with this, it was of interest to study in detail the ratio of $Cu(HDm)_2$ to alkali. The optical method was taken as the basis of study.

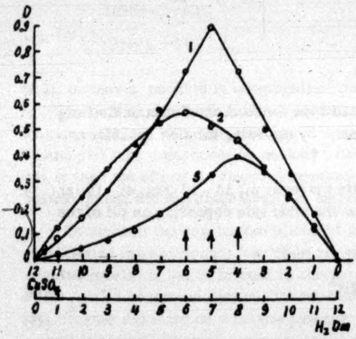

Fig. 7. Optical properties of equimolar mixtures of $CuSO_4$ and H_2Dm in neutral and alkaline media, pH: 1) 12.3, 2) 9 - 10, 3) 7 - 8.

In studying copper compound compositions in alkaline media, we prepared a series of equimolar solutions in which copper salt concentration varied from 1.2 moles/liter to zero and dimethylglyoxime concentration from zero to 1.2 moles/liter. In addition, to hold in solution copper hydroxide which does not react with dimethylgloxime, we added a third component: 5 ml 0.1 M sodium pyrophosphate solution mixed with hydrochloric acid, to the weakly alkaline solutions, and 1 ml of 0.5 M sodium tartrate to the strongly alkaline ones. Uniform pH was obtained by adding buffer mixture (phosphate or borate) in a quantity equal to half the total volume. Optical density was measured with a 5 cm layer thickness and with a 496 mμ wave length (Fig. 7).

As may be seen from Fig. 7, at pH 7 - 8 maximum optical density is observed for a solution with a 1:2 composition; i.e., at this acidity the stable compound is $Cu(HDm)_2$. On transition to more alkaline solutions, the height of the maximum increases and it also changes its location with regard to pH; this indicates formation of new strongly colored compounds. Thus, at pH about 10, maximum light absorption shifts in the direction of a solution with a 1:1 ratio, and then at pH equal approximately to 12, it again returns to solutions with larger dimethylglyoxime contents.

According to data from composition studies, the alkaline medium transformations may be described in the following manner. Replacement of the second hydrogen ion of dimethylglyoxime by copper ions is facilitated

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* No Table 5 appears in the original. Publisher.

TABLE 4

Optical Density of Mixtures of $CuSO_4$ Solutions with Dimethylglyoxime in Alkaline Media at Varying pH. $CuSO_4$ concentration = $2.5 \cdot 10^{-4}$ moles / liter, dimethylglyoxime concentration = $40 \cdot 10^{-4}$ moles/liter. Absorption layer thickness 5 cm.

Experiment number	pH	Optical density D		Concentration (moles / liter) $C \cdot 10^5$		$\log \frac{[Cu(Dm)_n]}{[Cu(HDm)_2]} + 2$
		at λ = 436 mμ	at λ = 465 mμ	$Cu(HDm)_2$	$Cu(Dm)_n$	
1	2	3	4	5	6	7
1	7.7	0.36	0.33	25	0	–
2	9.5	0.36	0.33	25	0	–
3	10.5	0.41	0.35	23.6	1.4	0.7732
4	10.75	0.43	0.36	23.0	2.0	0.9393
5	11.0	0.45	0.37	22.4	2.6	1.0647
6	11.25	0.50	0.39	20.5	4.5	1.3415
7	11.5	0.59	0.41	15.8	9.2	1.7651
8	11.75	0.69	0.45	11.9	13.1	2.0417
9	12.00	0.75	0.46	8.5	16.5	2.2881
10	12.25	0.78	0.48	7.9	17.1	2.3354
11	12.5	0.90	0.55	5.0	20.0	2.6021
12	12.75	1.02	0.58	–	–	–
13	12.9	1.0	0.54	–	–	–
14	13.0	0.95	0.50	–	–	–

in alkaline media. As a result of this, compounds of the disubstituted salt type are formed: CuDm or $Cu(Dm)_2^{--}$. Formation of complex anions in alkaline media is confirmed, particularly, by observing solution behavior on electrolysis.

Further, we present results of studying portions of the optical density curves at pH 10 - 12 (Fig. 4). Under these conditions the following equilibria are possible, shifting to one or the other side depending on pH of the medium:

$$Cu(HDm)_2 \rightleftarrows CuDm + 2H^+ + Dm^{--}. \tag{13}$$

$$Cu(HDm)_2 \rightleftarrows Cu(Dm)_2^{--} + 2H^+, \tag{14}$$

$$Cu(HDm)_2 \rightleftarrows Cu(Dm) + H^+ + HDm^-. \tag{15}$$

In the event compounds with a 1:1 ratio are formed [equations (13) or (15)], the latter reaction [equation (15) is the more probable], because according to the first acid dissociation constant for dimethylglyoxime (see above) at pH up to 12, dimethylglyoxime is mainly found in the H_2Dm or HDm^- form. For characteristics of equilibrium with significant or constant excess dimethylglyoxime, it is necessary to determine the relationship:

$$\frac{[Cu(Dm)_n]}{[Cu(HDm)_2]} = \underline{f}\,[H^+]. \tag{16}$$

Evidently, in the event of reaction by equations (13) or (14), the ratio, $\frac{[Cu(Dm)n]}{[CuHDm)_2]}$, will vary with the square of hydrogen ion concentration (n = 2), and in event reaction is by equation (15) this ratio will depend on hydrogen ion concentration to the first degree (n = 1).

For finding concentration of $Cu(HDm)_2$ or of compounds corresponding to disubstituted salt formulas, namely CuDm or $Cu(Dm)_2^{--}$, we may use a system of equations for mixtures of two colored components.

$$D_{\lambda_1} = (E'_{\lambda_1} C' + E''_{\lambda_1} C'')\, d, \tag{17}$$

$$D_{\lambda_2} = (E'_{\lambda_2} C' + E''_{\lambda_2} C'')\, d, \tag{18}$$

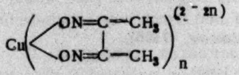
where D_{λ_1} is the optical density of the solution at a wave length λ_1; D_{λ_2} is optical density at wave length λ_2; E'_{λ_1} and E'_{λ_2} are molar extinction coefficients for one compound; E''_{λ_1} and E''_{λ_2} are analogous values for the second compound; C' and C'' are component concentrations; and $\underline{d}$ is layer thickness.

A series of solutions was prepared containing $2.5 \cdot 10^{-4}$ moles/liter $CuSO_4$ and $40 \cdot 10^{-4}$ moles/liter dimethylglyoxime with varying pH. As buffer we used a mixture of borax and caustic to the extent of 75 ml per 100 ml total volume. Optical density was measured with a 5 cm layer thickness in two portions of the spectrum — at 436 mμ and at 465 mμ. In calculating molar extinction coefficients by the formula $\log I_0/I = Ecd$ we used for $Cu(HDm)_2$ the optical density of solutions which did not change over the pH limits from 7.7 to 9.5, and for the assumed compounds CuDm or $Cu(Dm)_2^{--}$ the maximum optical density in alkaline media corresponding to solution 12 (Table 4). E_{436} and E_{465} for $Cu(HDm)_2$ were equal, respectively, to 290 and 260; analogous values for $Cu(Dm)_n$ were equal to 800 and 460. In Table 4, optical densities are given for the solutions and calculations made based on this residual value.

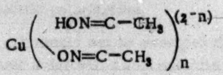
Fig. 8 was based on data of Table 4; from it we can see that the experimental points are close to the line having slope n = 1.

Thus, in accordance with the previously presented discussion, n = 1 and reaction at pH 10-12 goes by equation (15). These results are in agreement with earlier data on composition by methods of physico-chemical analysis.

Complexes of the disubstituted salt type, CuDm or $Cu(Dm)_2^{-}$, should be more stable as compared with complexes of the acid salt type, $CuHDm^+$ or $Cu(HDm)_2$. This should be expected based on comparing structural characteristics of compounds of the named type.



and



(it is, moreover, possible in compounds of the acid salt type to have coordination bonds between copper and the second oxime group). Greater stability should be expected for the neutral salt type compounds by analogy with a similar phenomena in the case of certain complex compounds of metals with hydroxy acids, diphenylthiocarbazone, and others.

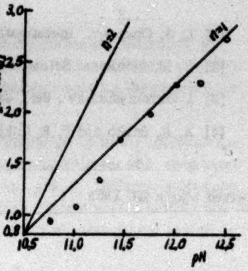


Fig. 8. Optical density of $CuSO_4$—dimethylglyoxime solution at varying pH in alkaline medium.

To confirm the conclusions presented above and also to characterize the compounds formed in a given system in a alkaline media, it was of interest to compare the stability of the named compound groups. Determining numerical values for the decomposition constant is extremely difficult because there are no standards characteristic of other copper complexes stable in alkaline media. However, a number of qualitative observations confirm the significant difference in stability of copper dioxime complexes formed in weakly acid and in alkaline media. This is clearly shown by the behavior of copper dioxime with certain reagents in various media. Particularly, by the characteristic behavior with hydroxyacid anions — such as tartaric and citric — with which copper forms complex compounds stable over the same limits as the copper dioximes. Experiments were set up in the following manner. 1 ml of a 0.1 M $CuSO_4$ solution was placed in a flask, a fourfold excess of dimethylglyoxime added as well as the same quantity of a tartaric acid salt. The contents of the flask were diluted to 50 ml by a buffer solution with known pH. Along with this, for comparison of the color, we prepared buffer solutions containing only the copper salt and dimethylglyoxime, as well as solutions containing only the copper salt and tartaric acid. It was found that weakly acid solutions containing copper, dimethylglyoxime, and tartaric acid turned a green color which was characteristic of tartaric acid copper complex — the more stable copper tartrate complex. And, on the contrary, alkaline solutions developed a reddish-brown color, characteristic of copper dioximes. The reddish-brown color did not change with high pH values even in presence of 50-fold excess of tartrate — the copper dioxime is the more stable. The same thing was observed on introducing citrates; however, significantly less of the latter is required for decomposing copper dioxime. As another example to confirm increased bond stability in copper dioximes formed in alkaline media, we note the behavior of $Cu(HDm)_2$ and ammonia. Ammonia alone does not decompose copper dioxime completely (alkaline medium). If, however, solution pH is decreased by addition of ammonium chloride, then complete decomposition of the copper dioxime takes place immediately.

SUMMARY

1. The reaction of complex formation between copper and dimethylglyoxime was studied at varying solution acidities.

2. It was shown that in weakly acid media and also in presence of excess Cu^{++} ions, a compound having the composition $CuHDm^+$ is formed in addition to the known compound $Cu(HDm)_2$. This follows from the increased solubility of $Cu(HDm)_2$ in presence of copper salts, physico-chemical investigation of the compound composition in solution, and also by observing the motion of the colored solution layer during electrolysis.

3. The dissociation constant $K = \frac{[Cu^{++}][HDm^-]}{[CuHDm^+]}$ for the $CuHDm^+$ complex was determined by two methods: via solubility of $Ni(HDm)_2$ in copper salts ($1.5 \cdot 10^{-10}$) and via an optical method ($0.8 \cdot 10^{-10}$).

4. It was shown that the solubility of $Cu(HDm)_2$ in alkalies is connected with formation of new intensively colored compounds, probably having the compositions: CuDm and $Cu(Dm)_2^{--}$.

5. The behavior of $Cu(HDm)_2$ with ammonia, tartrates, and citrates was studied, and it was shown that the change in composition in alkaline media is accompanied by increase in stability of the copper dioxime complexes.

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SOLUBILITY AND ADSORPTION OF AROMATIC ACIDS AS DEPENDENT ON NATURE AND POSITION OF SUBSTITUTENT GROUPS

N. F. Ermolenko and N. L. Lemets

Establishment of a relation between adsorption of organic acids and polarity of mixed media has been the subject of a large number of papers [1]. However, there are only a few studies in which the effect of structural characteristics of the organic acids on their solubility and adsorption was considered, [2].

Since it was shown that not only the polarity of the medium, but also the constitutional characteristics of the adsorbed molecules had an effect on the solubility and adsorption of organic acids, the problem was set in the present study to investigate the effect of nature and position of substituents in organic acids with regard to their adsorption on charcoal from solution in mixed organic media.

It was important, on the one hand, to establish the relationship between adsorption and solubility for these acids as dependent on their constitutional characteristics. On the other hand, it was necessary to explore the relationship between behavior of these acids in solution and the mixed medium's polarity, particularly its dielectric polarization.

It should not be expected that differences in location of the same substitutent group in the molecules of organic acids will affect solubility and adsorption of the acids to the same degree as differences in substituent group in the same location: both factors affect the polarity of the molecule as a whole; Different substituent groups, although they may occupy the same location in the molecule, can affect organic acid solubility and adsorption values to a significant degree by virtue both of differences in the moments of these groups as well as of differences in their tendency to form hydrogen bonds.

In the present study we took as the adsorbed organic acids: o-, m-, and p-nitrobenzoic, o- and p-chlorobenzoic, and p-hydroxybenzoic acids. All the acids were first carefully purified.

As mixed media we employed: $C_6H_6-CCl_4$; $C_6H_6-CHCl_3$; $C_6H_6-C_2H_5OH$; $C_6H_6-(CH_3)_2CO$; CCl_4-CHCl_3; $CCl_4-C_2H_5OH$; $CCl_4-C_6H_5NO_2$; $(CH_3)_2CO-C_2H_5OH$; $CHCl_3-C_2H_5OH$; $(CH_3)_2CO-C_6H_5NO_2$.

The solvents were likewise carefully purified; purity was checked by their constants. Ash-free activated wood charcoal was used as an adsorbent.

Among the constitutional characteristics studied were the effect of the nature of the substitutent and its location in the o- and p-positions in benzoic acid molecules with regard to solubility and adsorption.

Moreover, we studied the effect of substituent location in nitrobenzoic acids on adsorption and solubility. In all cases mixed media were used.

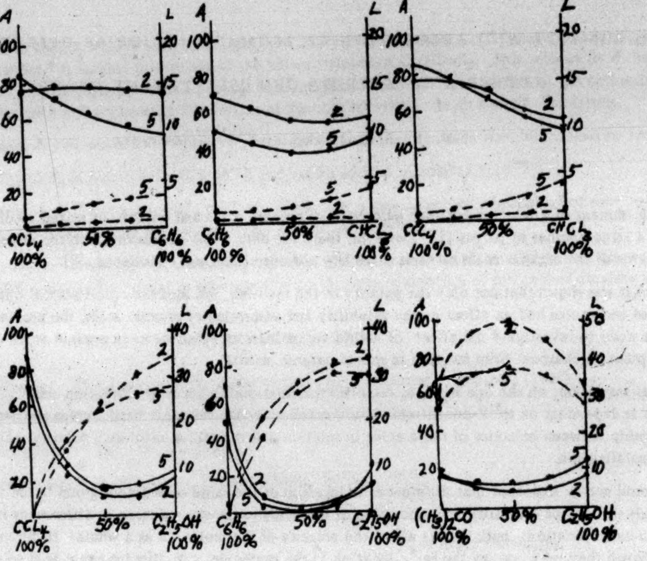
DISCUSSION OF RESULTS

1. Behavior of o-substituted benzoic acid in mixed media. Figures 1-6 present data on adsorption and solubility of o-chlorobenzoic and o-nitrobenzoic acids when using a number of mixed media.

o-Nitrobenzoic and o-chlorobenzoic acids appear significantly similar in their behavior in the $C_6H_6-CCl_4$, $C_6H_6-CHCl_3$, and CCl_4-CHCl_3 media. In all cases we observed complete correspondence between solubility and adsorption (Figs. 1-3). The similar relationship is connected with solvation of the acid by molecules of the mixed media.

With higher solubility of o-chlorobenzoic acid, which is connected with greater solvation by molecules of the medium, we observed smaller adsorption on charcoal. o-Chlorobenzoic acid, with a less polar functional group $-$ Cl ($\mu = 1.56 \cdot 10^{-18}$) $-$as compared with o-nitrobenzoic acid, which has the more polar nitro group ($\mu = 3.8 \cdot 10^{-18}$), is more solvated by molecules of the non-polar C_6H_6 and CCl_4 and consequently, the first acid's solubility is greater than that of the second, while their adsorbabilities are in the reverse ratio.

On transition to media with more polar components ($CHCl_3$) in the mixture, the solubility of o-chlorobenzoic



Figs. 1-6. Solubility (L) (dashed line) and adsorption (A) (solid line) for o-substituted benzoic acids in mixed media. 2) o-Nitrobenzoic acid; 5) o-chlorobenzoic acid.

acid increases more sharply than that of o-nitrobenzoic acid, in view of the fact that the first is solvated better by chloroform than the second (Figs. 2 and 3).

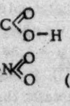
In mixed media in which one component is strongly polar (C_2H_5OH), the more polar o-nitrobenzoic acid is solvated better and therefore is more soluble than is the o-chlorobenzoic acid.

This difference exists more clearly as the solubility—composition curves approach the polar component and amounts to 4.7 g/100 ml in pure alcohol.

In pure benzene (Fig. 5) the less polar o-chlorobenzoic acid has greater solubility than the more polar o-nitrobenzoic acid by 1.24 g/100 ml, and its adsorption is less by 20.36%. On transition to alcohol the relation is changed in view of better solvation of the more polar o-nitrobenzoic acid by the polar component of the medium.

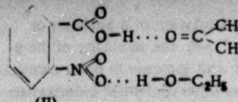
In view of the same structure and similar composition for the two o-substituted benzoic acids, the shapes of the solubility and adsorption curves for both acids are very similar to one another in the same mixed solvent. In a mixture of two polar solvents (Fig. 6) the mentioned acids behave similarly in solubility and adsorption. They differ only in a quantitative manner: the solubility of the more polar o-nitrobenzoic acid in a $(CH_3)_2CO-C_2H_5OH$ mixture is greater than that of the less polar o-chlorobenzoic acid by 5.7 g/100 ml in pure alcohol, by 3.6 g/100 ml in pure acetone, and by 12.4 g/100 ml in a 1:1 mixture of these materials.

For acids which contain a nitro or other group which can form hydrogen bonds in the o-position to the carboxyl group, it is possible to form the internal complex (I) in nonpolar media. This phenomenon is known as the "o-effect".



(I)

The significant increase in solubility of o-nitrobenzoic acid in a mixture of two polar components, $(CH_3)_2CO-C_2H_5OH$, with a 1:1 ratio of the latter, indicates possible formation of a more complicated acid—alcohol—acetone complex (II).

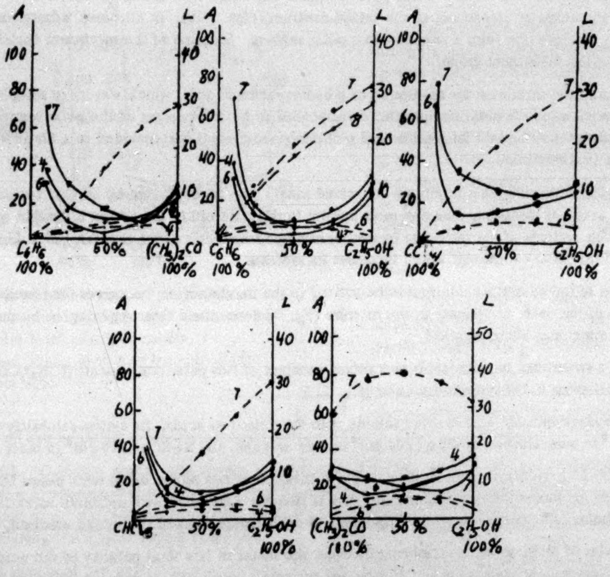


(II)

Maximum solvation (or solubility) of o-nitrobenzoic acid and o-chlorobenzoic acids in the indicated mixed medium, naturally corresponds to minimum adsorption; therefore, adsorption of the acids from mixed solvents passes through a minimum from pure acetone to pure alcohol, and the solubility through a maximum.

The differences observed in absolute solubility and adsorption values of the mentioned acids in the same media are caused by differences in absolute values for substitutent group polarities.

2. Behavior of p-substituted benzoic acid in mixed media. p-Substituted benzoic acid is very weakly solvated by nonpolar media (C_6H_6, CCl_4), as compared to benzoic acid. Consequently, it is poorly soluble in these media: solubility of p-nitrobenzoic acid amounts to 0.084 g/100 ml in C_6H_6 and 0.021 g/100 ml in CCl_4; that of p-chlorobenzoic acid is 0.118 g/100 ml in C_6H_6 and 0.059 g/100 ml in CCl_4; and finally, that of p-hydroxybenzoic acid is 0.52 g/100 ml in C_6H_6 and 0.435 g/100 ml in CCl_4.

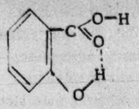


Figs. 7-11. Solubility (L) (dashed line) and adsorption (A) (solid line) for p-substituted benzoic acids in mixed media. Solubility data for o-hydroxybenzoic acid are given for comparison (Fig. 8). 4) p-Nitrobenzoic acid; 6) p-chlorobenzoic acid; 7) p-hydroxybenzoic acid; 8) o-hydroxybenzoic acid.

However, although the solubility of p-chlorobenzoic and p-nitrobenzoic acids does not increase significantly with increase in the polar component in mixed $C_6H_6-(CH_3)_2CO$ and $CCl_4-C_2H_5OH$ media, the solubility of p-hydroxybenzoic acid sharply increases with increase in polar component concentration in the medium.

This may be connected with the better conditions for forming hydrogen bonds between the medium's polar component and the COOH and OH groups of the hydroxybenzoic acid, (Figs. 7, 8, 9).

o-Hydroxybenzoic or salicylic acid is less soluble in the corresponding mixed medium ($C_6H_6-C_2H_5OH$) than p-hydroxybenzoic acid (Fig. 8); this may be related to the appearance in salicylic acid of cyclization or the o-effect (III) [3].



(III)

In all systems in which the medium was a mixture of a nonpolar or weakly polar component with a polar one (Figs 7-9), the solubility of the p-benzoic acid derivative taken by us increased with increase in polar component content in the mixed medium or with increase in its dielectric polarization ($P_{1,2}$)*.

In p-nitro and p-chlorobenzoic acids, the substituent functional group does not contain hydrogen able to form hydrogen bonds; consequently, if the polar component of the mixed medium likewise does not contain such hydrogen [$(CH_3)_2CO$], then solvation of such groups will be a minimum; this will result in low solubility of these acids in the stated media.

However, for p-nitrobenzoic acid in the $C_6H_5OH-C_2H_5OH$ system, formation of hydrogen bonds between the C_2H_5OH molecule and the $-\mathrm{N}\Big\langle{}^{O}_{O}$ group (or its solvation) hinders dimerization of the alcohol; as is known, the bond energy for alcohol dimer formation is 6.2 kcal/mole, whereas that for water is 4.5 kcal/mole. This naturally does not exclude the possibility [4] of dimerizing the alcohol molecules and other dipolar molecules by simple interaction of the dipoles.

Adsorption of p-substituted benzoic acids goes through a minimum with change in the ratio of the polar or weakly polar to the nonpolar component in the mixed medium (Figs. 7-10). In all cases, adsorption of these acids fell sharply on transition from a nonpolar to a polar solvent. Location of the minimum varies somewhat with the nature of the substituent group.

The location of the minimum for adsorption of p-hydroxybenzoic acid, which was more soluble in a mixed medium with a predominately polar component, corresponded to 65-75% content of the polar component in the mixture; the adsorption minimum for p-nitro- and p-chlorobenzoic acids corresponded to a 35-50% content of the polar component in the mixture.

Passage of adsorption through a minimum for mixed media may be explained by several factors. If the fundamental factor is taken as solvation, then one must assume in this case either the action of double solvation (polar and nonpolar portions of the molecule by corresponding components of the medium) or an association of the molecules of the polar component which increases its moment.

The location of the adsorption minimum corresponding to the maximum on the curves for change in dielectric polarization of the polar component in the mixture (P_2), is determined to a large degree by the degree of solvation of the molecules being adsorbed.

Behavior of p-substituted benzoic acids in a mixed medium of two polar components [$(CH_3)_2CO-C_2H_5OH$] differs from its behavior in the systems discussed (Fig. 11.)

Here the p-hydroxybenzoic acid is more soluble than the other two acids; its excess solubility corresponds to 27-28 g/100 cm^3 in pure alcohol, 26-27 g/100 cm^3 in pure acetone, and 34-35 g/100 cm^3 in their 1:1 mixture.

The solubility of p-hydroxybenzoic acid in a mixed medium of two polar components passes through a maximum; the adsorption passes through a minimum; this is likewise associated with optimum solvation of the acid molecules at a molar ratio rather close to 1:1 for the two polar components of the mixed medium.

In the behavior of p-chloro and p-nitrobenzoic acids, the factor of low total polarity of the acid molecule (in the sense of electrostatic reaction of the dipoles and the small possibility of forming hydrogen bonds with the molecules of the medium) leads to the condition that the solubility and the adsorption both change slightly with change in the polar component ratio in the medium.

3. Effect of substitutent position in benzoic acid on its solubility and adsorption. The position of the same

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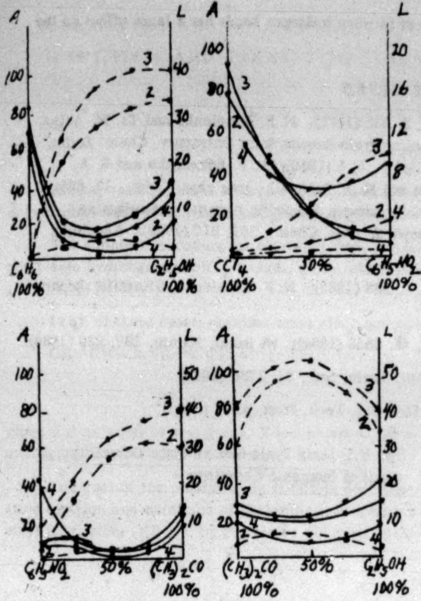
* The dielectric polarization value for a mixed medium is obtained, as we know, starting from the Mosotti equation:

$$P_{1,2} = \frac{\epsilon-1}{\epsilon-2} \cdot \frac{C_1M_1 + C_2M_2}{d_{1,2}} = C_1P_1 + C_2P_2,$$

where $P_{1,2}$ is the dielectric polarization of the mixture, ϵ is the dielectric constant of the mixture, M_1 and M_2 are the molecular weights of the components of the mixed medium, C_1 and C_2 are the mole fractions of the components, $d_{1,2}$ is the density of the medium, and P_1 and P_2 are the dielectric polarizations for the components.

The value of the dielectric polarization of a polar component with a nonpolar second component, in terms of P_1, is $P_2 = \dfrac{P_{1,2} - C_1P_1}{C_2}$.



Figs. 12-15. Effect of nitro-group position in nitrobenzoic acids on solubility (L) (dashed line) and adsorption (A) (solid line) in mixed media.
2) o-Nitrobenzoic acid; 3) m-nitrobenzoic acid;
4) p-nitrobenzoic acid.

substituent in a benzoic acid derivative changes the molecule polarity and consequently should affect its solubility and behavior in solution.

In this case we studied solubility and adsorption of o-, m-, and p-nitrobenzoic acid in the mixed media: $C_6H_6-C_2H_5OH$, $CCl_4-C_6H_5NO_2$, $(CH_3)_2CO-C_2H_5OH$, and $(CH_3)_2CO-C_6H_5NO_2$.

In view of the vanishingly small solubility of p-nitrobenzoic acid in CCl_4, it was only possible to study its behavior in mixtures of two polar or one polar and nonpolar component, (Figs. 12-15).

A general characteristic of p-nitrobenzoic acid is its lower solubility both in nonpolar and in polar media. Consequently, the solubility of p-nitrobenzoic acid changes only slightly, passing through a small maximum in traversing certain systems [$C_6H_6-C_2H_5OH$ and $(CH_3)_2CO-C_2H_5OH$]. Solubilities of o- and m-nitrobenzoic acids sharply increase with transition through mixed media ($C_6H_6-C_2H_5OH$, $CCl_4-C_6H_5NO_2$; Figs. 12 and 13) from the nonpolar component to the polar one; this indicates increased solvation of the acid in the more polar medium. In the direction of the more polar component, dielectric polarization of the mixture ($P_{1,2}$) also increases.

In the mixed medium $C_6H_6-C_2H_5OH$, adsorption of o-, m-, and p-nitrobenzoic acids passes through a minimum lying in a region corresponding to a 1:1 component ratio in the medium, and corresponding to the highest conditions of acid solvation, because the ethyl alcohol dipole on dimerization evidently becomes stronger [5] (Fig. 12).

In the $CCl_4-C_6H_5NO_2$ system, the change in adsorption is inverse to the change of solubility, i.e., the more the solubility of a nitrobenzoic acid falls, the more its adsorption increases (Fig. 13). Similar changes in solubility and adsorption of o-, m-, and p-nitrobenzoic acids were observed also with change in component ratio of mixtures in the $C_6H_5NO_2-(CH_3)_2CO$ system (Fig. 14).

In mixed media of two polar components (Fig. 15), the solubility of all three nitrobenzoic acids passes through a clearly expressed maximum at a 1:1 ratio of $(CH_3)_2CO$ to C_2H_5OH in the mixture. A particularly sharp solubility maximum is shown by the more soluble, and consequently more solvated, o- and m- acids. Evidently, for them it is more characteristic to form hydrogen bonds both with alcohol molecules and with acetone, as was shown above.

Adsorption of all three nitrobenzoic acids passes through a minimum, lying at the same component ratio in the medium; this confirms our suppositions with regard to the role of solvation in the processes of solution and adsorption of acids.

SUMMARY

The relationship of solubility and adsorption was studied for benzoic acid derivatives as dependent on the nature and location of the substituent, as well as the polarity of the mixed media.

1. It was shown that an inverse relationship exists between adsorption of o-, m-, and p-substituted benzoic acids on charcoal from solutions in mixed organic media and their solubility. If the adsorption curve passes through a maximum, the solubility curve passes through a minimum.

2. The character of the substituent group in benzoic acid derivatives has a larger effect on solubility and adsorption than does the position of one and the same substituent in the acid.

3. The functional group polarity and its possibility of forming hydrogen bonds has a large effect on the adsorption and solubility of benzoic acid derivatives.

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SYNTHESIS AND TRANSFORMATION OF α-METHYLVINYL BUTYL ETHER. II.

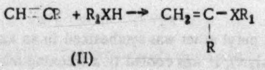
M. F. Shostakovsky and E. P. Gracheva

Among various unsaturated compounds having reactive properties, compounds whose structures contain one or two substituents on a vinyl group carbon are of great interest.

The simplest procedure for obtaining these compounds (I, II) is by reacting acetylene and monosubstituted acetylenic hydrocarbons with alcohols, acids, mercaptans, amines, and other compounds containing labile hydrogen [1,2,3,4].

In all of these cases, reaction takes place according to the scheme:

$CH\equiv CH + R_1XH \rightarrow CH_2=CH-XR_1$ (I)

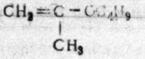


$CH\equiv CR + R_1XH \rightarrow CH_2=C(R)-XR_1$

(II)

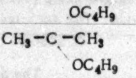
where R is an alkyl or aryl group, X is a hetero O, N, S, or other atom, and R_1 is the radical from the acid, alcohol, mercaptan, etc.

The goal of the present study is further development of the A.E.Favorsky and M.F.Shostakovsky [2] vinylation reaction and extension of the synthesis of α-substituted vinyl ethers, particularly the synthesis of α-methyl vinyl butyl ether (III) and its derivative dimethyldibutoxyketal (IV).



$CH_2=C(CH_3)-OC_4H_9$

(III)



$CH_3-C(OC_4H_9)_2-CH_3$

(IV)

Compound (III), like other representatives of this homologous series [5] is of interest for studying reactivity with regard to addition and hydrolysis reactions.

Preparation of α-substituted vinyl compounds indicates that existence of reaction between methylacetylene and alcohol requires more severe conditions than were established by A. E. Favorsky and M. F. Shostakovsky for the corresponding reaction with acetylene.

This observation is in complete agreement with the proposal of M. F. Shostakovsky with regard to reactivity of chemical compounds, which depends on the number of reactive centers in the molecule (the number of functional groups with labile hydrogen).

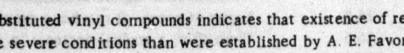
Based on reaction adding butyl alcohol to α-methylvinyl butyl ether under the influence of mineral acid (HCl), it was established that this reaction is exothermal and leads to forming dimethyldibutoxyketal (IV) in good yield. As regards procedures for obtaining this ketal, some data can be found in the literature on this question.

Claisen [6] described a general method for preparing acetals of aldehydes and ketones based on reacting the latter with orthoformic esters in an ether solution.

A. E. Arbuzov [7], working on obtaining the ketal of acetone (according to the Claisen procedure), improved the cited synthesis by showing that this reaction was catalytic and brought the addition of mineral acid (HCl, H_2SO_4) to its necessary catalytic minimum.

Nieuwland and coworkers [8] describe in a number of papers the preparation of ketals based on alkylacetylenes and alcohols in presence of mercury oxide and BF_3.

The authors of the present paper made the observation that the α-methylvinyl butyl ether prepared* and its derivative – dimethyldibutoxyketal – readily hydrolyze in presence of water or dilute acids:



$$CH_2=C(CH_3)-OC_4H_9 + HOH \xrightarrow{H^{\cdot}} CH_3COCH_3 + C_4H_9OH$$

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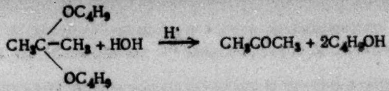
* Not previously reported in the literature.



$$CH_3C(OC_4H_9)_2{-}CH_3 + HOH \xrightarrow{H^+} CH_3COCH_3 + 2C_4H_9OH$$

In the literature, hydrolysis of α-substituted vinyl ethers is discussed in a number of studies by A. M. Butlerov [9], A. P. Eltekov [10], and A. E. Favorsky [11]. A. E. Arbuzov [7] studied in detail the dissociation of ketals under action of dilute sulfuric acids. Claisen [6] noted the ease of hydrolyzing the ketals he prepared.

EXPERIMENTAL

1. Initial substances and method of synthesis

Butyl alcohol (b.p. 117°, d_4^{20} 0.830, n_D^{20} 1.3988) and methylacetylene (b.p. −28°) were used as raw materials for synthesis of α-methylvinyl butyl ether and its ketal.

Methylacetylene was prepared by the method of Hurd and Spence [12], by brominating propylene and subsequently splitting out two molecules of hydrogen bromide. The methylacetylene obtained in this manner was dried by passage through a column filled with calcium chloride and condensed in a receiver cooled with dry ice in a Dewar flask.

α-Methylvinyl butyl ether was synthesized in an autoclave. Before charging with the corresponding quantity of alcohol (with catalyst), it was cooled in a freezing mixture (ice, salt) to −10 to −15°.

Working with methylacetylene was performed by cooling it with dry ice in an ampoule, previously weighed, which was introduced into the autoclave containing butyl alcohol and 10% powdered potassium hydroxide.

2. Synthesis of α-methylvinyl butyl ether (III)

Into a rotating Bergius-type autoclave, having 2.5 liter volume and fitted with electrical heating, thermocouples, and an acetylene pressure gauge, we charged 111 g (1.5 mole) butyl alcohol, 50 g (1.2 mole) methylacetylene, and 10 g powdered potassium hydroxide. The autoclave was heated for a 14 hour period at a temperature of 248-250°.

Time	Autoclave temperature, (°C)	Autoclave pressure (atm)
0	0	7.0
0 hr 35 min	100	10.6
1 hr 10 min	135	15.2
2 hr 30 min	182	25.5
3 hr 30 min	225	38.0
4 hr 20 min	238	50.0
5 hr 05 min	348	58.0
	248	50.5
	250	43.0
	250	40.5

The dependence of pressure on temperature is given in the table.

It can be seen from the table that with increase in temperature a significant increase in autoclave pressure begins to occur. It reaches a maximum at 250° (58 atm). Thereafter, a gradual decrease in pressure was observed despite constancy of heating temperature.

After heating, the autoclave was cooled, and unreacted methylacetylene collected in a trap placed in a Dewar flask containing dry ice. 5.4 g methylacetylene was collected. The remaining reaction mass was transferred from the autoclave into a flask which was set in freezing mixture (snow + salt).

Distillation of the reaction mass was performed in a flask, with herringbone dephlegmator, in a Wood's metal bath.

The following fractions were collected: 1) b.p. 105-107° (745.5 mm), 121.2 g; 2) b.p. 117-118° (745.5 mm), 27.4 g; tarry residue, 11.8 g.

Investigation of fractions. The first fraction with a b.p. of 105-107° (745.5 mm) was washed 8 times with water, dried with potash, and distilled in a column with an effeciency of 20 theoretical plates. In all, 90.7 g of the substance distilled at 111-112° (751 mm).

n_D^{20} 1.4111; d_4^{20} 0.7955. Found: M 112.6 (cryoscopically). MR$_D$ 35.80; %C 73.97; H 12.34. $C_7H_{14}O$. Calculated: M 114; MR$_D$ 36.05; %C 73.70; H 12.40.

Hydrolysis of α-methylvinyl butyl ether. 20 g of the substance and 30 ml 1% H_2SO_4 solution were placed into a conical flask fitted with a ground stopper. The reaction mass was shaken for a period of 1 hour at room temperature, i.e., for the time necessary for the ether layer to disappear, after which the acid was neutralized with calcined potash. The reaction product was salted out, extracted with ether, dried, and distilled in a flask with a herringbone dephlegmator on a water bath.

After distilling the solvent, a fraction was collected with b.p. 50-70°; this was dried over calcined potash and redistilled. After treating the separated substance with 2,4-dinitrophenylhydrazine, yellow-orange crystals precipitated; after three recrystallizations from alcohol, these had a 127.7° m.p., which corresponds to the 2,4-dinitrophenylhydrazone of acetone. Mixture tests gave no depression. The literature value [13] for the m.p. is 128°.

Thus, investigating the fraction having a 111-112° b.p. (751 mm) indicated that as a result of reacting methylacetylene with butyl alcohol in presence of KOH, synthesis of α-methylvinyl butyl ether occurs with a yield 75.8% of the theoretical.

3. Synthesis of Dimethyldibutoxyketal (IV).

Into a three-necked flask, fitted with mercury seal, reflux condenser, thermometer, and mechanical stirrer, we placed equimolecular quantities of α-methylvinyl butyl ether (11.4 g – 0.1 mole) and butyl alcohol (7.4 g – 0.1 mole). The mixture was thoroughly agitated for a 30-40 minute period and then catalyst (concentrated HCl) was added to the extent of two drops (0.04 g) at room temperature. After catalyst was added, the reaction mass temperature began to rise rapidly to 45-47° and then slowly fell to the initial room temperature.

In all, distillation separated 14.4 g of a substance having a 69-70° b.p. (24 mm); tarry residue was 2.7 g.

Investigation of the substance with b.p. 69-70° (24 mm). The product obtained was dried over calcined potash and distilled a second time at 70° (24 mm).

n_D^{20} 1.4150; d_4^{20} 0.8363. Found M 185.6 (cryoscopically); MR_D 56.21. %C 70.12, 70.02; H 12.83, 13.05. $C_{11}H_{24}O_2$. Calculated: M 188; MR_D 56.6; %C 70.2; H 12.8.

Hydrolysis of dimethyldibutoxyketal. A 25 g quantity of the substance and 60 ml of 1% H_2SO_4 solution were charged into an Erlenmeyer flask. The reaction mixture was shaken for a period of 1 hour, after which the acid was neutralized with a small amount of calcined potash, and the hydrolysis products distilled.

A broad fraction with 50-73° b.p. was collected in the amount of 2.77 g; this was dried with potash and treated with 2,4-dinitrophenylhydrazine; yellowish-red crystals precipitated, which after recrystallization from alcohol had m.p. 126.9°, which corresponds to the 2,4-dinitrophenylhydrazone of acetone.

Characteristics of the fraction boiling at 70° (24 mm) indicate that as a result of the interchange reaction between methylvinyl butyl ether and butyl alcohol in the presence of traces of HCl, synthesis of dimethyldibutoxyketal takes place with an 81% yield.

SUMMARY

1. Conditions were found for synthesis of α-methylvinyl butyl ether with a yield 75% of the theoretical.

2. Conditions were found for synthesis of dimethyldibutoxyketal with a yield 81% of the theoretical.

3. Hydrolysis of α-methylvinyl butyl ether or of dimethyldibutoxyketal leads to formation of the ketone and alcohol.

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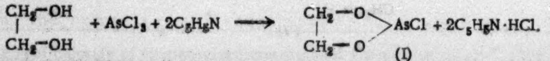
* See Consultants Bureau English Translation, p. 1209.

ETHYLENEGLYCOLARSENOUS ACID ESTERS

Gilm Kamai and Z. L. Khisamova

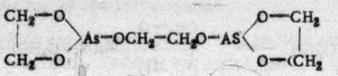
Detailed investigation of cyclic derivatives of arsenous acid was started in our laboratory in 1950 [1-2]. Cyclic esters of ethyleneglycolarsenous acid have not been studied by anyone. In the present paper, we present data obtained by us in studying acyl chlorides and mixed esters of ethyleneglycolarsenous acid, containing five-membered rings.

By action of an equimolar quantity of arsenic trichloride on ethylene glycol in an absolute ether medium in the presence of anhydrous pyridine, we synthesized the cyclic acid chloride of ethyleneglycolarsenous acid (I) as the main reaction product according to the equation:



(I)

It was also found that in this reaction, in addition to the acid chloride, the complete ethylene glycol ester of arsenous acid was formed (II).

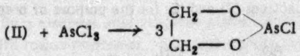


(II)

Experiments we performed on reacting the acid chloride of ethyleneglycolarsenous acid with ethylene glycol in presence of pyridine in an absolute ether medium led to the same final result. Thus, it was shown that ester (II) forms as a result of secondary reaction.

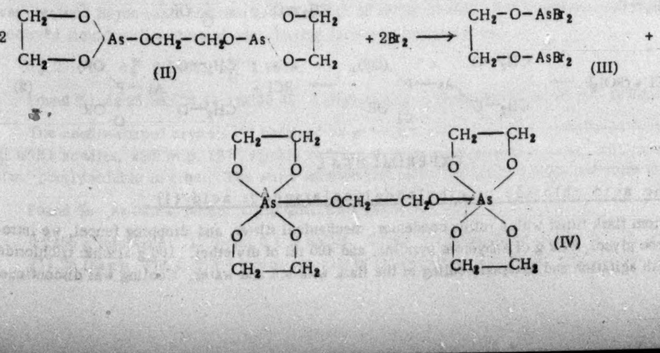
The complete ethylene glycol ester of arsenous acid (II) is also obtained in a very satisfactory yield of about 89-92% by direct reaction of arsenous anhydride on ethylene glycol at a temperature of 140-150°. This reaction is reversible; with excess water the ester completely hydrolyzes, forming arsenous anhydride.

Under the action of equimolar quantities of arsenic trichloride on (II), the acid chloride of ethyleneglycolarsenous acid (I) forms almost quantitatively according to the equation:



(I)

The ethylene glycol ester of arsenous acid (II) does not react on heating with methyl iodide and does not add sulfur or cuprous bromide. Its bromination reaction proceeds very unusually. Instead of the expected addition of two bromine molecules, exactly only half of the calculated quantity, i.e., one bromine molecule, adds in the given reaction. In this reaction, a very interesting transformation with complex radical rearrangement takes place. We previously [1] gave the following scheme for the course of reaction.

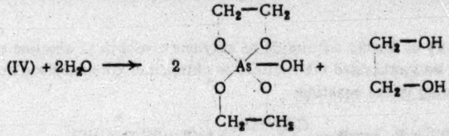


(II) (III) (IV)

Formation of the acid bromide (III) under conditions of the experiment was actually shown. The acid bromide was a green-colored liquid with a mustard odor and b.p. 86° at 11 mm.

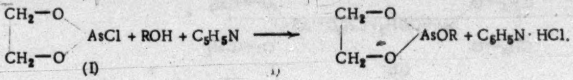
The second compound containing pentavalent arsenic separated by us formed glistening crystals with a 127° m.p. — readily soluble in many organic solvents and in water; it did not hydrolyze in the cold. Its aqueous solution had an acid reaction and could be titrated by 0.1 N NaOH solution. Doubts arose concerning the hypothetical structure previously given by us [1] for substance (IV). Further study showed that this compound was diethyleneglycolarsenous acid (V), described by Englund [3]. However, in contrast to Englund's preparation, our sample melted at 127°, and not 120°; its molecular weight, determined by the Rast method, was not double, but actually was close to the double value in a bromoform solution.

Formation of diethyleneglycolarsenous acid probably is via hydrolysis of the above-mentioned hypothetical compound (IV):


(IV) + 2H₂O ⟶ 2
CH₂—CH₂
O O
As—OH +
O O
CH₂—CH₂
CH₂—OH
CH₂—OH

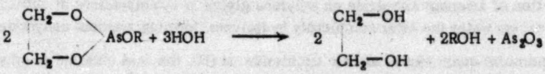
(V)

By reacting the acid chloride of ethyleneglycolarsenous acid (I) with the corresponding absolute alcohol in presence of pyridine in an ethyl ether medium, we synthesized various mixed esters of ethyleneglycolarsenous acid according to the following scheme:

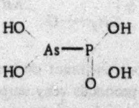

CH₂—O
CH₂—O
AsCl + ROH + C₅H₅N ⟶
(I)
CH₂—O
CH₂—O
AsOR + C₅H₅N · HCl.

In this manner we separated methyl, ethyl, n-propyl, n-butyl, n-hexyl, n-heptyl, n-octyl, nonyl, phenyl, and cyclohexyl esters of ethyleneglycolarsenous acid.

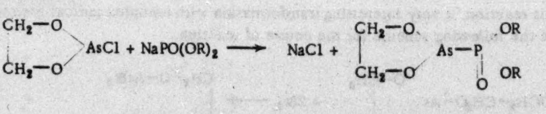
Under action of water, the above-cited esters decompose relatively readily, evolving heat and forming the corresponding alcohol, ethylene glycol, and arsenous anhydride:


2
CH₂—O
CH₂—O
AsOR + 3HOH ⟶ 2
CH₂—OH
CH₂—OH
+ 2ROH + As₂O₃

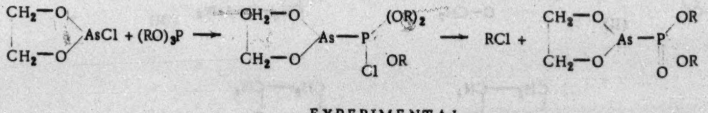
We made attempts to perform reactions (1) and (2) for the purpose of preparing a derivative of the hypothetical imaginary acid:


HO
HO
As—P
OH
OH
O

but they remained unsuccessful.


CH₂—O
CH₂—O
AsCl + NaPO(OR)₂ ⟶ NaCl +
CH₂—O
CH₂—O
As—P
OR
OR
O

(1)


CH₂—O
CH₂—O
AsCl + (RO)₃P ⟶
CH₂—O
CH₂—O
As—P
(OR)₂
OR
Cl
⟶ RCl +
CH₂—O
CH₂—O
As—P
OR
OR
O

(2)

EXPERIMENTAL

Preparation of the acid chloride of ethyleneglycolarsenous acid (I)

Into a round-bottom flask fitted with a reflux condenser, mechanical stirrer, and dropping funnel, we introduced 37.5 g of ethylene glycol, 87.2 g of anhydrous pyridine, and 400 ml of dry ether. 100 g arsenic trichloride was added dropwise with agitation and external cooling of the flask with ice and water. Cooling was discontinued after the arsenic chloride was all introduced and the reaction mixture was heated on a water bath for a period of one hour and allowed to stand overnight. On the next day the ethereal solution was separated from the precipitate by decantation and the residue washed 3 times with absolute ether. The filtrate, after distilling the solvent, was subjected to vacuum distillation. As a result of distillation at 11 mm, the following fractions were separated: 1) 61.3 g with b.p. 70-76°; 2) 6.5 g with b.p. 76-160°; and 3) 10.3 g with b.p. 160-195°.

By doubly distilling the first fraction, we separated a substance with b.p. 71-72° at 11 mm, melting point 44-45°.

Found %: As 44.10; Cl 20.99. $C_2H_4O_2AsCl$. Calculated %: As 44.05; Cl 20.82.

The separated cyclic acid chloride of ethyleneglycolarsenous acid formed white, glistening, needle-shaped crystals readily soluble in ether, benzene, toluene, dichloroethane, and dioxane. The acid chloride immediately hydrolyzes in water, evolving heat and forming As_2O_3 (found %: As 75.21; calculated % As 75.73).

From the third, high-boiling fraction, we obtained a substance with a 166-167° b.p. at 4 mm (II), a colorless, viscous liquid:

d_4^{20} 1.8951; n_D^{20} 1.5433; MR_D 56.18; calculated 56.61. Found %: As 45.28. $C_6H_{12}O_6As_2$. Calculated %: As 45.40.

Preparation of the complete ethylene glycol ester of arsenous acid (III)

1) From the acid chloride of ethyleneglycolarsenous acid and ethylene glycol. The acid chloride of ethyleneglycolarsenous acid was added to a solution of 4.2 g of ethylene glycol and 10.4 g pyridine in 200 ml dry ether with mechanical agitation and cooling. After removing pyridine salts the filtrate was subjected to distillation. The main fraction had a b.p. of 166-167° at 4 mm.

2) From arsenous anhydride and ethylene glycol. 60 g arsenous anhydride and 86.4 g ethylene glycol were taken in a round-bottom Arbuzov flask. The flask was heated on an oil bath at 140-150° for a 30 minute period. A water aspirator was then connected for removing water formed in this reaction. After removing the water under vacuum and double distillation, we obtained 80.2 g of a fraction with b.p. 160-161° at 2 mm (92.4%).

Found %: As 45.47, 45.66. $C_6H_{12}O_6As_2$. Calculated %: As 45.40.

Action of arsenic trichloride on the complete ethylene glycol ester of arsenous acid. 15 g complete ethylene glycol ester of arsenous acid was placed in a round-bottom flask having a reflux condenser and dropping funnel. 6 g arsenic trichloride was added to it dropwise. At the end the contents of the flask were heated on a water bath for a 30 minute period. After cooling, the reaction mixture was vacuum distilled. The main fraction had b.p. 66-67° at 9 mm and m.p. 44-45°.

Found %: As 43.98; Cl 20.67. $C_2H_4O_2AsCl$. Calculated %: As 44.05; Cl 20.82.

Saponification of ester (II). 25 g arsenous acid ethylene glycol ester was boiled with 50 ml water for a period of 1 hour in a round-bottom flask with reflux condenser. The white precipitate separated was arsenous anhydride.

Found %: As 75.62. As_2O_3. Calculated %: As 75.73.

Action of bromine on ester (II). 28 g bromine was added through a dropping funnel to 51 g ester dissolved in carbon tetrachloride. The reaction flask was cooled externally by snow. On adding each drop of bromine, an energetic reaction took place, with evolution of heat. Bromination was continued until appearance of a light yellow color. Needle-shaped crystals separated from the solution on standing. On the second day the crystals were filtered, pressed, and washed with carbon tetrachloride. The filtrate was subjected to vacuum distillation. 32.2 g was obtained in the main fraction having a b.p. of 86° at 11 mm. The substance separated was a slightly greenish colored liquid with a mustard odor, having lachrymatory properties.

d_0^0 2.6079; d_0^{20} 2.5668; n_D^{20} 1.6568.

Found %: As 28.38, 28.41; Br 60.39. $C_2H_4O_2As_2Br_4$. Calculated %: As 28.30; Br 60.36.

The needle-shaped crystals (V) obtained by us were then repeatedly recrystallized from hot toluene. Gleaming, white needles, with m.p. 127°, soluble in toluene, benzene, dioxane, acetone, chloroform, ethyl alcohol, and water; poorly soluble in ether. The water solution had an acid reaction (Congo red turns intense blue).

Found %: As 35.62, 35.63. $C_4H_9O_5As$. Calculated %: As 35.42.

0.2255 g substance: 10.75 ml 0.1 N NaOH. Found: equimolecular weight 210.82. Found M 210.41, 211.25 (Rast); 378.4, 375.6 (cryoscopically in bromoform). $C_4H_9O_5As$. Calculated: M 212.03.

By reacting 1.5 g brucine in a methyl alcohol solution with 0.807 g diethyleneglycolarsenous acid (V), we obtained a salt with m.p. about 204°, which corresponds to the data of Englund [3].

Found %: As 11.82, 11.63. $C_{23}H_{26}O_4N_2(C_2H_4O_2)_2AsOH \cdot CH_3OH$. Calculated %: As 11.75.

Preparation of ethyleneglycolarsenous acid methyl ester

20 g of the acid chloride of ethyleneglycolarsenous acid (I) dissolved in 50 ml ethyl ether was added through a dropping funnel to 3.8 g methyl alcohol, 9.2 g anhydrous pyridine, and 250 ml absolute ethyl ether cooled to 0°. After adding the entire quantity of acid chloride, the reaction mixture was heated on a water bath for a period of one hour. On the next day the pyridine hydrochloride was filtered off and washed 3 times with dry ether. After distilling the solvent, the remaining liquid was vacuum distilled. 8.6 g of a fraction was obtained with b.p. 50-51° at 11 mm. Ethyleneglycolarsenous acid methyl ester was a mobile liquid. It was readily hydrolyzed by water, forming arsenous anhydride.

Preparation of other esters of ethyleneglycolarsenous acid was conducted by the method described, starting with the corresponding alcohol, 9.2-9.3 g dry pyridine, and 20 g of the acid chloride of ethyleneglycolarsenous acid (I) in 200-300 ml ethyl ether.

The esters obtained were colorless liquids (beginning with the hexyl ester they had a thick consistency), and odorless (except for the nonyl ester, which had a pleasant odor).

Data for the esters prepared are given in the table.

Esters of Ethyleneglycolarsenous Acid

Ester	Formula	Alcohol taken for reaction (g)	Ester yield (g)	B.p., °C	Pressure (mm)	d_0^0	d_0^{20}	n_D^{20}	MR$_D$		As content (%)	
									Found	Calculated	Found	Calculated
Methyl	$C_3H_7O_3As$	3.8	8.6	50-51	11	1.6453	1.6310	1.4935	29.25	29.41	44.72	45.09
Ethyl *	$C_4H_9O_3As$	9.5	19	61-62	11	1.5031	1.4784	1.4788	34.50	34.03	41.54 41.71	41.61
n-Propyl	$C_5H_{11}O_3As$	7	–	74-75	12	1.4188	1.3923	1.4762	39.33	38.64	38.85	38.60
n-Butyl	$C_6H_{13}O_3As$	8.7	11	93	16	1.4024	1.3764	1.4785	42.82	43.26	36.31	36.00
n-Hexyl	$C_8H_{17}O_3As$	12	17	120-121	10	1.3033	1.2813	1.4742	51.86	52.49	31.63	31.72
n-Heptyl	$C_9H_{19}O_3As$	13.7	21.8	130-131	11	1.2671	1.2465	1.4736	56.37	57.14	29.80	29.94
n-Octyl **	$C_{10}H_{21}O_3As$	15.2	14	110	2	1.2449	1.2250	1.4737	61.44	61.73	28.41	28.34
n-Nonyl	$C_{11}H_{23}O_3As$	17	15.6	117-118	2	1.2240	1.2041	1.4748	–	–	27.33	27.03
Cyclohexyl ***	$C_8H_{15}O_3As$	8.8	–	118	11	1.4270	1.4044	1.5070	–	–	31.84	32.00
Phenyl	$C_8H_9O_3As$	11	6.3	143-144	12	1.5687	1.5440	1.5716	–	–	32.70	32.85

* 16.4 g pyridine and 35 g acid chloride (I) were taken for the reaction.

** 6.7 g pyridine taken for reaction.

*** 6.9 g pyridine and 15 g acid chloride (I) were taken for reaction.

Experiment on reacting ethyleneglycolarsenous acid methyl ester with methyl iodide

5 g ethyleneglycolarsenous acid methyl ester and 8 g methyl iodide were heated in a flask with reflux condenser on a water bath for a period of 6 hours. On distillation, according to data on boiling points and refractive indices, the initial substances were recovered. It was not possible to separate any other individual substance.

Action of bromine on ethyleneglycolarsenous acid ethyl ester

5 g ethyleneglycolarsenous acid ethyl ester and 20 ml of carbon tetrachloride were placed in a round-bottom flask of 50 ml capacity. 4.4 g bromine was added through a dropping funnel. Vigorous heating was observed. The carbon tetrachloride was distilled at normal pressure. The remaining liquid was distilled under vacuum. The main fraction boiled at 72-73° at 14 mm.

The addition product was a heavy, light-yellow colored liquid.

d_0^0 2.2152; d_0^{20} 2.1767; n_D^{20} 1.5880.

Found %: As 22.09; Br 46.69. $C_4H_9O_3AsBr_2$. Calculated %: As 22.04; Br 47.03.

Action of the acid chloride of ethyleneglycolarsenous acid on the butyl ester of phosphorous acid

15 g tributylphosphite dissolved in 200 ml ethyl ether was taken in a round-bottom flask fitted with reflux condenser and dropping funnel. After cooling to −13° (ice + salt), 10.3 g acid chloride of ethyleneglycolarsenous acid was then added, half diluted with ether. The exchange reaction takes place very vigorously. The reaction mass at first is noticeably yellow, and then becomes brown. A precipitate of red phosphorus separated on standing. The precipitate was filtered. The filtrate was subjected to distillation. After removing the ether at normal pressure, a fraction was obtained boiling at 117-121° (d_4^{20} 0.8099, n_D^{20} 1.4015), which corresponded to butyl alcohol. Subsequently, the following fraction was separated by vacuum distillation: b.p. 140° at 5 mm; d_0^0 1.1185, n_D^{20} 1.4333. The substance contains arsenic and phosphorus, but it readily decomposes forming a black residue.

Reacting the acid chloride of ethyleneglycolarsenous acid with the Na-derivative of diethylphosphorous acid

200 ml dry ethyl ether and 4.1 g metallic sodium were placed in a reaction flask. 24.5 g diethylphosphorous acid was then added from a dropping funnel.

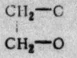
A 30 g quantity of the acid chloride of ethyleneglycolarsenous acid, half diluted with ether, was added dropwise with external cooling to the Na-derivative of diethylphosphorous acid. The contents of the flask first turned yellow during the addition, and at the end acquired a brick-red color. The residue −sodium chloride− was filtered off. After drying, its pure weight was 9.9 g (theoretically required 10.3 g). Strong decomposition took place during distillation under vacuum. It was not possible to separate individual substances.

SUMMARY

1. It was shown that by reacting ethylene glycol with arsenic trichloride in an absolute ether medium and in the presence of pyridine, it was possible to obtain the acid chloride of ethyleneglycolarsenous acid and the complete ethylene glycol ester of arsenous acid.

2. A simpler and more convenient method for preparing the ethylene glycol ester of arsenous acid was developed by means of reacting ethylene glycol with arsenous anhydride.

3. The bromination reaction of the arsenous acid ethylene glycol ester was studied. In this reaction an acid bromide having the composition $[-CH_2OAsBr_2]_2$ was separated, and also diethyleneglycolarsenous acid.

4. Cyclic mixed esters were synthesized having the composition  $\begin{matrix} CH_2-C \\ | \\ CH_2-O \end{matrix} \rangle AsOR$ and their reactions and properties described.

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TERTIARY TRIHYDRIC ALCOHOLS OF THE ACETYLENIC SERIES AND THEIR TRANSFORMATIONS

III. POTASSIUM PERMANGANATE OXIDATION

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It was shown in our earlier papers [1,2] that the A.E.Favorsky reaction – the reaction of acetylene with ketones in a dry ether medium in presence of powdered potassium hydroxide – could be varied to prepare tertiary trihydric alcohols of the acetylenic series, if a ketoalcohol were used instead of the ketone, and an acetylenic alcohol used in place of acetylene.

In systematically studying chemical transilformations of acetylenic glycerols, we encountered the need to have a clear picture of the manner in which their oxidation by potassium permanganate occurred.

In the last ten or fifteen years, enough papers have already appeared in the chemical literature dealing with the question of oxidation of triple bonds in acetylenic hydrocarbons, alcohols, and particularly, in glycols. Without doubt, these introduced some clarity into the question being discussed here by us. However, these investigations, in the first place, frequently did not have a systematic character, and, in the second place, of the hydroxyl-containing acetylene derivatives, they refer almost exclusively to γ-glycols; they hardly touch at all upon questions of oxidizing acetylenic α-glycols, erythritols, and trihydric alcohols.

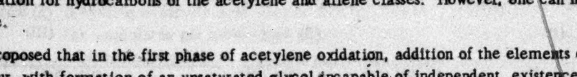
Attempts to formulate a scheme for oxidation of triple bonds by potassium permanganate were already undertaken by E. E. Vagner, who, in his classical investigations on oxidizing olefins, tried also to give a probable scheme of oxidation for hydrocarbons of the acetylene and allene classes. However, one can hardly agree entirely with his scheme.

Vagner proposed that in the first phase of acetylene oxidation, addition of the elements of hydrogen peroxide to it would occur, with formation of an unsaturated glycol incapable of independent existence, which on hydration would be transformed into a hydrated form of a glycollic aldehyde; the latter would then lose water, and, depending on the order in which this water evolution occurred, either oxalic or acetic acid would be formed.

V. N. Krestinsky and M. K. Kelbovskaya [3] undertook attempts to separate any neutral products from the oxidation of acetylenic hydrocarbons. They oxidized acetylene, phenylacetylene, methylethylacetylene, and tertiary butylacetylene. However, they were not able to separate any neutral products on the basis of which it would be possible to formulate conclusions on the specific mechanism of this process. They only separated acids.

The authors proposed that the primary products of adding the elements of the oxidant to the triple bond evidently undergo hydrolysis, forming acids corresponding to breakdown at the triple bond location.

It seems to us that it is simpler to assume for acetylenic bond oxidation, following Vagner, the formation of neutral glycols in a first phase which, naturally, in view of the energetic oxidizing medium, are not able to undergo all the transformations Vagner describes; having a double bond, they are more readily split because of the presence of two hydroxyl groups, and are immediately subjected to further oxidative action by the potassium permanganate. Addition of two more water residues to the double bond occurs, with subsequent separation of water and formation of a diketone, which then oxidizes further to the acid usually obtained on oxidation of acetylene or acetylenic hydrocarbons.



$$\mathrm{C{\equiv}C} \xrightarrow{O + H_2O} \mathrm{COH{=}COH} \xrightarrow{O + H_2O} \mathrm{C(OH)_2{-}C(OH)_2} \xrightarrow{-2H_2O} \mathrm{C{=}O{-}C{=}O}$$

In case there are hydroxyl groups adjacent to the triple bond present in the molecule, then the oxidation process is somewhat complicated by secondary reactions as a result of which neutral substances may appear among the oxidation products, in addition to acids.

DuPont [4] and V. N. Krestinsky and N. Persiantseva [5], on oxidizing tetramethylbutynediol with potassium permanganate, obtained acetone and oxalic acid, in addition to α-hydroxyisobutyric acid. This circumstance forced them to assume the presence of two tautomeric forms in tetramethylbutynediol.

However, none of the facts given in the literature confirms the accuracy of this assumption, with the exception of the fact that oxalic acid and acetone are obtained on oxidation. However, their formation can be completely explained without assuming tautomeric forms. On the other hand, experimental material has been accumulating during recent years which, like the data obtained by us and published below, directly shows the absence of these tautomeric forms, both from tertiary acetylenic γ-glycols and from other structurally similar acetylene hydroxyl derivatives.

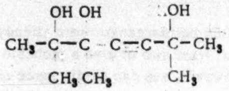
T. I. Temnikova and P. A. Tikhomolov [6] performed the oxidation of tetratolylbutynediol with chromic anhydride in acetic acid; they were able to separate a cyclic o-diketone.

P. A. Tikhomolov and A. E. Druzhinin [7] under the same conditions, likewise obtained a corresponding o-diketone by oxidizing tetraphenylbutynediol.

Yu. S. Zalkind and P. S. Bataev [8] separated free diketone after oxidizing tetraphenylbutynediol ethers with chromic anhydride.

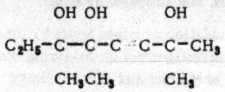
S. A. Zonis [9] studied the oxidizing action of manganese triacetate on acetylenic γ-glycols. He showed that in oxidizing ditertiary acetylenic γ-glycols of the aromatic or aliphatic-aromatic series, manganese triacetate acts as an acetylating agent on the triple bond; a diacetyle derivative of a substituted dihydrofurane is formed. In case manganese triacetate acts on ditertiary γ-glycols of the aliphatic series, oxidation proceeds otherwise, and leads to destruction of the carbon chain. On oxidizing a disecondary acetylenic γ-glycol with the same oxidant, Zonis obtained acetylenic diketones.

In the present study, we oxidized 6 tertiary alcohols of the acetylenic series with potassium permanganate:



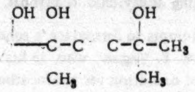
$CH_3-\underset{CH_3}{\overset{OH}{C}}-\underset{CH_3}{\overset{OH}{C}}-C\equiv C-\underset{CH_3}{\overset{OH}{C}}-CH_3$

(I)

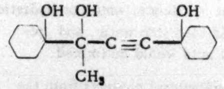


$C_2H_5-\underset{CH_3}{\overset{OH}{C}}-\underset{CH_3}{\overset{OH}{C}}-C\equiv C-\underset{CH_3}{\overset{OH}{C}}-CH_3$

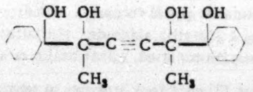
(II)



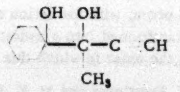
(III)



(IV)



(V)



(VI)

2,3,6-Trimethylheptyne-4-triol-2,3,6 (I). Acetone and dimethylacetylcarbinol were obtained, and acetic, formic, oxalic, and α-hydroxyisobutyric acids.

3,4,7-Trimethyloctyne-5-triol-3,4,7 (II). We obtained acetone, methyl ethyl ketone, and methylethylacetylcarbinol, as well as acetic, formic, oxalic, and α-hydroxyisobutyric acids.

2,5-Dimethyl-5-(1-hydroxycyclohexyl)-pentyne-3-diol-2,5 (III). We obtained acetylcyclohexanol, cyclohexanone, and acetone, as well as formic, acetic, oxalic, and α-hydroxyisobutyric acids.

2,4-Di-(1-hydroxycyclohexyl)-butyne-3-ol-2 (IV). We obtained acetylo yclohexanol, cyclohexanone, and acetic, oxalic, α-hydroxyhexahydrobenzoic, and adipic acids.

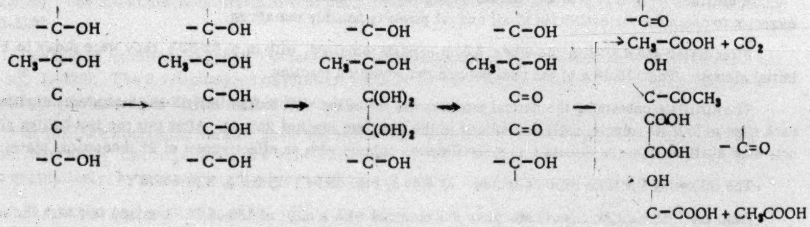
2,5-Di-(1-hydroxycyclohexyl)-hexyne-3-diol-2,5 (V) (in acetone solution). We obtained acetylcyclohexanol, and cyclohexanone, and formic, acetic, oxalic, and adipic acids.

2-(1-Hydroxycyclohexyl)-butyne-3-ol-2 (VI). We obtained acetylcyclohexanol and cyclohexanone; formic, acetic, oxalic, and adipic acids.

Thus, oxalic acid was obtained in all six cases of oxidation. Its formation in the sixth, last, case could be explained by the presence of tautomeric forms as proposed by DuPont, Krestinsky, and Persiantseva. It has been shown in our laboratory that tertiary trihydric alcohols of the ethylenic series, where the possibility of the cited tautomerization is completely excluded, also give oxalic acid on oxidation by potassium permanganate.

Consequently, the matter is not one of tautomerization. Starting with the data obtained by us, and also based on the fact that a number of authors, in oxidizing some acetylenic γ-glycols, were able to separate saturated diketones, it is necessary to assume that the acetylenic bond oxidizes in the very same manner in hydroxyl-containing acetylene derivatives as it does in acetylenic hydrocarbons. This scheme in the case of permanganate oxidation does not differ in principle from the scheme of oxidizing double bonds in ethylenic hydrocarbons, as developed by Vagner, i.e., in the first reaction phase the elements of hydrogen peroxide add to the triple bond. The unsaturated glycol formed, which is then subjected to further oxidative action, again adds the elements of hydrogen peroxide to the double bond, and thus transforms into a diketone. Subsequent oxidative attack, evidently, is directed at carbon bonds both between carbon atoms having carbonyl oxygen atoms, and between carbon atoms on one of which there is a carbonyl oxygen, and on the other a hydroxyl group. Oxidation takes place likewise even at bonds between carbon atoms both of which have hydroxyl oxygen.

The material just discussed may be expressed by the following scheme:



At the same time, judging from the quantity of α-hydroxyisobutyric acid (or α-hydroxyhexahydrobenzoic acid, respectively) which is separated as a result of oxidation to the extent of more than half a mole per mole of substance oxidized (see table), it should be concluded that the oxidant action is mainly directed at the bond between carbons carrying ketonic oxygens.

Alcohol oxidized	Quantity of substance (g)	Obtained		NaOH (g) used in titrating the volatile acids, calculated per mole of substance oxidized
		α-hydroxyisobutyric acid (g), calculated per mole of substance oxidized	Oxalic acid (g), calculated per mole of substance oxidized.	
I	16.49	52.7	6.7	8.57
II	13.9	59.0	13.6	11.1
III	16.9	56.1	42.8	7.38
IV	17.4	67.6*	23.5	2.15
V	6.0	–	46.5	2.96
VI	4.7	–	14.3	8.0

* The acid was α-hydroxyhexahydrobenzoic.

Moreover, it follows from the table presented that oxalic acid is formed comparatively slightly in the case when the acetylenic alcohol being oxidized contains an aliphatic radical, and that formic and acetic acids are formed to a significantly greater extent. The same results are obtained in the case where a mono-substituted hydroxyl derivative of acetylene is oxidized. Introducing a cyclic alcohol group as the substituting radical somewhat increases oxalic acid formation. Here the quantity of volatile acid is significantly decreased; this can be seen from the quantity of sodium hydroxide used for titrating the volatile acids, the quantity of which has been calculated per mole of substance oxidized.

As regards formic acid, its formation should be attributed somewhat to the partial oxidation of acetone, which is either obtained as a result of reaction or is introduced into the reaction as a solvent. The ability of acetone to be oxidized by potassium permanganate was shown by Evans and Nicoll [10], who found that in acid or neutral media acetone was oxidized by permanganate to acetic acid and CO_2. Formation of the latter in this case must be considered as a result of further oxidation of formic acid.

From (VI), formic acid is formed because of direct oxidation of the α-glycol at the triple bond.

Adipic acid is formed from (IV) and (V) as the result of subsequent partial oxidation of cyclohexanone.

EXPERIMENTAL

Oxidation of 2,3,6-trimethylheptyne-4-triol-2,3,6 (I).

20 g of 2,3,6-trimethylheptyne-4-triol-2,3,6, with m.p. of 82-83°, dissolved in 100 ml of water, was introduced into a liter flask fitted with mechanical stirrer, and then 1134 ml of 3% potassium permanganate solution was added slowly dropwise (based on calculating 3 active oxygen atoms per alcohol molecule). Oxidation took place at room temperature. After addition of all the potassium permanganate solution, the transparent solution was filtered from the precipitated manganese dioxide deposit; the precipitate was washed several times with hot water.

A distillate of netural products was distilled from the filtrate and the acid salts extracted by ether in an extractor to complete the extraction of all neutral products possibly remaining.

After drying and distilling the ether, 3.51 g crystals remained, with m.p. 82-83°; they were shown to be the initial alcohol. Thus, 16.49 g of the triol entered the oxidation reaction.

The distillate containing the neutral products was salted out with sodium sulfate and repeatedly distilled, each time to half its volume, until the volume of the distillate reached 200 ml. After this the low-boiling products were distilled from the distillate in a rectification column with an effectiveness of 22 theoretical plates.

The following fractions were collected: 1) 0.55 g, b.p. 53-54°; 2) 2.8 g, b.p. 54-78°.

From the first fraction a semicarbazone was obtained with a m.p. of 185-187°. A mixed test with the semicarbazone of known acetone melted at 185-187°. In addition, a 2,4-dinitrophenylhydrazone was obtained with m.p. 124-126°; a mixed test with the 2,4-dinitrophenylhydrazone of known acetone did not give a melting point depression.

The aqueous fraction remaining after distilling the readily volatile neutral products was saturated with sodium sulfate and extracted with ether in an extractor until neutral products were completely extracted. The ether extracts were dried and the residual liquid, after distilling the ether, (1.2 g) distilled at normal pressure. The following fractions were obtained:

1) B.p. to 135°; n_D^{20} 1.4130; 2) b.p. 135-139°, n_D^{20} 1.4162.

From the second fraction we obtained a semicarbazone in the form of transparent crystals which after recrystallization from methyl alcohol melted at 160-161° and did not give a depression on melting with the semicarbazone of known dimethylacetylcarbinol.

The acid salts were acidified with hydrochloric acid and the volatile acids steam distilled. The steam-distilled distillate containing volatile acids was neutralized with 180.95 ml standardized sodium hydroxide solution (0.1052 N); this corresponds to 0.7602 g sodium hydroxide. The presence of formic acid was shown by obtaining a calomel precipitate, and the presence of acetic acid — by the cacodyl oxide reaction.

The non-volatile acids were neutralized with sodium hydroxide, heated to 70-80°, and, using a saturated calcium chloride solution, oxalic acid was precipitated as its calcium salt, from which 0.6 g oxalic acid was obtained with a m.p. of 101-102°. Mixture tests with known oxalic acid did not show depression. The filtrate after separating the calcium oxalate salt was acidified with hydrochloric acid and extracted with ether in an extractor. The separated crystals (4.7 g) after recrystallization from benzene melted at 79° and did not give a depression on fusion with known α-hydroxyisobutyric acid.

Thus, as a result of oxidizing 2,3,6-trimethylheptyne-4-triol-2,3,6, acetone and dimethylacetylcarbinol were obtained from the neutral products, and acetic, formic, oxalic, and α-hydroxyisobutyric acids from the acid products.

Oxidation of 3,4,7-trimethyl-octyne-5-triol-3,4,7 (II).

1053 ml of 3% potassium permanganate solution was slowly added dropwise to 20 g of freshly distilled triol with a b.p. of 135-136° at 3-4 mm, dissolved in 100 ml water (based on calculating three active oxygen atoms per octynetriol molecule).

Separation and investigation of oxidation products was performed in the same manner as in the previous experiment; 6.1 g triol was recovered, consequently 13.9 g of the substance entered the reaction.

The following fractions were taken from the column on distilling the distillate containing neutral products: 1) 0.8 g with b.p. 53-56°; 2) 0.5 g with b.p. 56-71°; 3) 0.8 g with b.p. 71-81°.

A semicarbazone and a 2,4-dinitrophenylhydrazone were obtained from the first fraction; these melted at 185-187° and 124-125°, respectively, and corresponded to acetone.

A 2,4-dinitrophenylhydrazone with m.p. 112-113° was obtained from the second and third fraction; this corresponds to the 2,4-dinitrophenylhydrazone of methyl ethyl ketone (mixture tests).

5.2 g of a substance was separated from the solution after distilling the readily volatile products in the column; on distillation of this, the following fractions were collected: 1) 0.4 g with b.p. up to 60°; 2) 0.2 g with b.p. from 60 to 80°, n_D^{20} 1.3848; 3) 1.2 g with b.p. 80-146°; 4) 1.6 g with b.p. 146-149°, n_D^{20} 1.4210; residue 0.6 g.

The second fraction corresponds to methyl ethyl ketone according to its refractive index (literature data: n_D^{20} 1.3839). The 2,4-dinitrophenylhydrazone of methyl ethyl ketone was obtained from this fraction and melted at 112-113°.

According to its refractive index, the fourth fraction corresponds to methylethylacetylcarbinol (literature data: n_D^{20} 1.4220). The 2,4-dinitrophenylhydrazone melts at 107-108° and corresponds to the 2,4-dinitrophenylhydrazone of methylethylacetylcarbinol (mixture test).

The distillate containing volatile acids was neutralized with 185.92 ml standardized sodium hydroxide solution (0.0970 N); this corresponds to 0.7214 g sodium hydroxide. Presence of formic and acetic acids was shown qualitatively, by preparation of calomel and cacodyl oxide.

0.95 g oxalic acid with m.p. of 101-102° (mixture test) and 4.1 g α-hydroxyisobutyric acid melting at 79° (mixture test) were separated from the non-volatile acids).

Thus, as a result of oxidizing 3,4,7-trimethyloctyne-5-triol-3,4,7, acetone, methyl ethyl ketone, and methylethylacetylcarbinol were obtained among the neutral products and acetic, formic, oxalic, and α-hydroxyisobutyric acids among the acid products.

Oxidation of 2,5-dimethyl-5-(1-hydroxycyclohexyl)-pentyne-3-diol[illegible],5 (III).

20 g of 2,5-dimethyl-5-(1-hydroxycyclohexyl)-pentyne-3-diol-2,5 (m.p. 87-88°) was dissolved in 100 ml water, and then 934 ml 3% potassium permanganate solution was gradually added dropwise (based on calculating three active oxygen atoms per alcohol molecule).

Separation and investigation of oxidation products was similar to the previous experiments. 3.1 g of unreacted starting substance was recovered (m.p. 87-88°).

A fraction weighing 0.7 g with b.p. 52-53° was distilled in a column from the distillate containing neutral products; its semicarbazone was obtained by the Zelinsky method. The crystals, recrystallized from methyl alcohol, melted at 185-187°; mixture tests with the semicarbazone of known acetone did not show melting point depression.

The acetone obtained was also confirmed by preparing its 2,4-dinitrophenylhydrazone, which had a m.p. of 124-125° (mixture test).

From the solution remaining after distilling the acetone, 8.4 g of a substance was then extracted with ether. As a result of distillation (at normal pressure) these fractions were obtained: 1) 1.2 g with b.p. 32-150°; 2) 1.4 g with b.p. 150-190°; 3) 4.85 g with b.p. 190-204°.

A semicarbazone having a m.p. of 160-163° was obtained from the second fraction; after recrystallization from methyl alcohol it melted at 165-166°, and did not show a depression in melting point when fused in a mixture with the semicarbazone of known cyclohexanone.

A semicarbazone was likewise obtained from the third fraction; recrystallized from methyl alcohol, it melted at 194-195° and did not give a depression on fusion with the semicarbazone of known acetylcyclohexanol.

A distillate containing volatile acids was distilled from the acid salts after acidification with hydrochloric acid; in neutralizing this 142.2 ml standardized sodium hydroxide solution (0.0970 N) was used, which corresponds to 0.5517 g sodium hydroxide. Presence of formic and acetic acids was shown by qualitative reactions — formation of precipitated calomel and cacodyl oxide.

3.2 g oxalic acid with a m.p. of 101-102° and 4.2 g α-hydroxyisobutyric acid with a m.p. of 79° (mixture test) were extracted from the non-volatile acids.

Thus, in oxidizing 2,5-dimethyl-5-(1-hydroxycyclohexyl)-pentyne-3-diol-2,5, acetone, cyclohexanone, acetylcyclohexanol, acetic acid, formic acid, oxalic acid, and α-hydroxyisobutyric acid were obtained.

Oxidation of 2,4-di-(1-hydroxycyclohexyl)-butyne-3-ol-2 (IV)

20 g of the substance and 100 ml water were placed in a liter flask and 790 ml 3% potassium permanganate solution added dropwise (based on calculating three active oxygen atoms per alcohol molecule). 2.6 g unreacted 2,3-di-(1-hydroxycyclohexyl)-butyne-3-ol-2 was recovered (m.p. 107-108°).

6.5 g of substance was separated from the distillate containing neutral products; in distillation of this, we obtained the fractions: 1) 0.25 g with b.p. 40-150°; 2) 1.5 g with b.p. 150-170°; n_D^{20} 1.4507; 3) b.p. 170-196°, 3.0 g.

The second fraction corresponds to cyclohexanone (literature data: n_D^{20} 1.4520). A semicarbazone was obtained from it — white crystals with m.p. 166-167° (mixture test)

From the third fraction (b.p. 170-196°) after a second distillation, we separated a fraction with b.p. 188-192° and n_D^{20} 1.4683, containing acetylcyclohexanol. (For known acetylcyclohexanol, n_D^{20} 1.4700). A semicarbazone was obtained in the form of transparent needle-shaped crystals melting at 194-195° (from methyl alcohol).

The distillate with volatile acids was neutralized with 44.16 ml standardized sodium hydroxide solution (0.1052 N); this corresponds to 0.1855 g sodium hydroxide. Presence of acetic acid was shown by obtaining cacodyl oxide. Formic acid was not detected.

After distilling volatile acids in a distillation flask, an oily layer floated on the surface which did not steam-distill, and which crystallized on cooling. The crystals (4.6 g), when recrystallized from benzene, melted at 105-106°. According to its melting point this acid corresponds to α-hydroxyhexahydrobenzoic acid [11].

The molecular weight of the acid with m.p. 105-106° was determined by titration.

0.0707 g substance: 7.7 ml 0.0675 N $Ba(OH)_2$. Found: M 139.5. $C_7H_{12}O_3$. Calculated M 144.

The barium salt was obtained; it contained 32.09% Ba. $(C_7H_{11}O_3)_2Ba$. Calculated %: Ba 32.45.

After separating the α-hydroxyhexahydrobenzoic acid from solution, oxalic acid was separated (1.6 g, with m.p. 101-102°), and 2.9 g of crystals which after recrystallization from ethyl acetate, melted at 150-152° and were shown to be adipic acid (mixture test).

Thus, as the result of oxidizing 2,4-di-(1-hydroxycyclohexyl)-butyne-3-ol-2, cyclohexanone and acetylcyclohexanol were obtained, together with the acids: α-hydroxyhexahydrobenzoic, oxalic, adipic, and a small amount of acetic.

Oxidation of 2,5-di-(1-hydroxycyclohexyl)-hexyne-3-diol-2,5 (V)

In view of the fact that this erythritol is not soluble in water, we performed its oxidation in acetone. 8.5 g of the erythritol having a m.p. of 161-162° and 300 ml acetone previously distilled over potassium permanganate were introduced into the flask. Then potassium permanganate (8.7 g) was introduced with continuous agitation and in small portions over a 6 hour period (based on calculating three active oxygen atoms per molecule of the erythritol). Oxidation took place at room temperature. The translucent acetone solution was filtered from precipitated manganese dioxide; the latter was washed with acetone and then several times with hot water. After distilling the acetone, a liquid (6.3 g) remained in the flask from which crystals separated (1.7 g); these were shown to be the starting unoxidized erythritol (mixture test). The liquid, after separating unreacted erythritol, was distilled at normal pressure. We collected the fractions: 1) 0.6 g with b.p. 130-150°; 2) 0.95 g with b.p. 150-155°, n_D^{20} 1.4510; 3) 0.7 g with b.p. 155-195°; 4) 1.3 g with b.p. 195-200°, n_D^{20} 1.4692; residue 0.8 g.

The second fraction is cyclohexanone; its semicarbazone was obtained by the Zelinsky method. The crystals after recrystallization melted at 165-166°, and did not give a depression when fused with the semicarbazone obtained from known cyclohexanone.

The fourth fraction was shown to be acetylcyclohexanol; a semicarbazone was obtained from it with m.p. 194-195° (mixture test).

The water solution which contained the acid salts was extracted with ether in an extractor for extraction of possibly unoxidized erythritol. After this the supplemental ether was distilled, and 0.8 g crystals with m.p. 161-162° was separated, corresponding to the initial erythritol. Consequently, 2.5 g of unoxidized substance was recovered from the 8.5 g taken for the reaction. The water solution was acidified with hydrochloric acid, and the volatile acids steam distilled. The distillate was neutralized with a sodium hydroxide solution. 121.8 ml sodium hydroxide (0.1176 N) was used in neutralization — corresponding to 0.5737 g sodium hydroxide.

Presence of acetic and formic acids was shown qualitatively, although the calomel precipitate was rather small.

0.9 g oxalic acid with a m.p. of 101-102° and 0.3 g adipic acid with m.p. 151-152° were separated from the non-volatile acids.

Thus, by oxidizing 2,5-di-(1-hydroxycyclohexyl)-hexyne-3-diol-2,5, cyclohexanone, acetylcyclohexanol, oxalic acid, acetic acid, traces of formic acid, and adipic acid were obtained (the last as the product of oxidation of cyclohexanone).

Oxidation of 2-(1-hydroxycyclohexyl)-butyne-3-ol-2 (VI)

6 g of the glycol (m.p. 67-68°) dissolved in 50 ml water was placed in a flask and 377 ml 3% potassium permanganate solution (three active oxygen atoms per glycol molecule) gradually added. Separation and investigation of reaction products were similar to the foregoing. 1.3 g of a thick liquid which crystallized on standing was recovered from the reaction; the crystals melted at 67° and were unreacted α-glycol.

2.8 g of a substance was separated from the distillate which contained the neutral products; on its distillation, the following fractions were collected.

1) 0.3 g, b.p. 40-150°; 2) 0.3 g, b.p. 150-175°; 3) 0.5 g, b.p. 175-190°; 4) 1.1 g, b.p. 190-204°; residue 0.4 g.

The second fraction was cyclohexanone. A semicarbazone was prepared from it having a m.p. of 165-166° (mixture test).

The fourth fraction appeared to be acetylcyclohexanol; its semicarbazone melted at 194-195° (mixture test).

The distillate with volatile acids was titrated using sodium hydroxide solution (0.1176 N). 47.7 ml was used in neutralization — corresponding to 0.2247 g sodium hydroxide. Presence of formic and acetic acids were shown by qualitative reactions. Formic acid gave a voluminous calomel precipitate.

Oxalic acid (0.4 g) with m.p. 101-102° was separated from the nonvolatile acids, and mixture tests with commercial known oxalic acid did not show a depression. Moreover, 1.2 g of a liquid with a sharp acid odor was separated; it partly crystallized after lengthy standing. The separated crystals melted at 128-132°. In view of the small quantity, we were not able to purify it. In all probability, it was adipic acid.

Thus, on oxidizing 2-(1-hydroxycyclohexyl)-butyne-3-ol-2, cyclohexanone and acetylcyclohexanol were separated from the neutral products, and oxalic, acetic, and formic acids sere separated from the acids.

SUMMARY

1. It is not necessary to consider that tautomeric forms actually exist, either for tertiary acetylenic γ-glycols as assumed by DuPont, Krestinsky, and Persiantseva, or for other tertiary polyhydric alcohols of the acetylenic series.

2. Tertiary acetylenic alcohols, α- and γ-glycols, glycerols, and erythritols are oxidized by potassium permanganate, evidently first of all to diketones, at the triple bond.

3. Oxidation does not halt at the stage of forming diketones and goes farther, on the one hand at bonds between carbons one of which has carbonyl oxygen and the other a hydroxyl; this causes formation of oxalic acid. On the other hand, it takes place on the bond between carbons having hydroxyl groups. The oxidation reaction mainly takes place on the bond between carbons with carbonyl oxygen, i.e., at the location of the triple bond in hydroxyl-containing acetylene derivatives.

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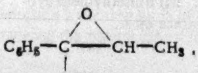
INVESTIGATIONS IN THE FIELD OF CYCLIC ACETALS OF HYDROXYCARBONYL COMPOUNDS

IV. DIMETHYLBENZOYLCARBINOL METHYL LACTOLIDE/AND ITS TRANSFORMATIONS

T. Temnikova and N. Almashi

Methyl lactolides of α-ketoalcohols (α-methoxy or α-hydroxy) have hardly been studied. The methyl lactolide of methylbenzoylcarbinol (I)

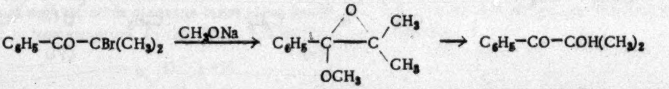


(I)

the first example of this class of compounds whose structure has been rigidly established, was obtained comparatively recently by T. I. Temnikova and E. N. Kropacheva [1]. Study of the properties of this interesting compound is naturally difficult in view of its great tendency to polymerize. It was of interest to extend our investigation on chemical transformations of methyl lactolides of α-ketoalcohols, using a more stable substance as a basis; it could be expected, theoretically, that methyl lactolides of methylbenzoylcarbinol homologs which contained other hydrocarbon groups in place of the methyl would show less tendency to polymerize.

In the present research, we performed an investigation of the properties of dimethylbenzoylcarbinol methyl lactolide (II) and of its changes on reaction with various reagents.

The methyl lactolide of dimethylbenzoylcarbinol was prepared by the action of dry sodium methylate on α-bromoisoprppyl phenyl ketone in absolute ether:



(II) (III)

Dimethylbenzoylcarbinol methyl lactolide (1-methoxy-1-phenyl-2,2-dimethylethylene oxide) was a rather mobile liquid which did not change on extended storage.

Hydrolysis of the cyclic oxide occurs on heating the methyl lactolide (II) with 5% aqueous H_2SO_4 solution, and dimethylbenzoylcarbinol (III) is obtained.

To confirm the correctness of conclusions on structure for the substance obtained by reacting CH_3ONa with α-bromoisopropyl phenyl ketone, we performed spectrochemical investigations on it in the ultra-violet, based on our chemical data, and compared its absorption spectrum (Fig. 1, curve I) with the spectrum of dimethylbenzoyl carbinol (Fig. 1, curve II). The absorption spectrum of the substance obtained by reaction of CH_3ONa with α-bromoisopropyl phenyl ketone does not have an absorption maximum in the λ = 270-290 mμ region; this indicates the absence of a carbonyl group in it. The substance absorbs only in the shorter wave region, on account of the benzene ring present in it. The absorption spectrum of dimethylbenzoylcarbinol is characterized by two maxima: at a λ = 287 mμ and 320 mμ, because of the presence of a benzoyl group in this substance.

Thus, spectrochemical study confirms as correct the conclusion that the substance obtained from reacting sodium methylate with α-bromoisopropyl phenyl ketone had a methoxy oxide (II) structure.

On reacting an aqueous-alcoholic solution of semicarbazide acetate with methyl lactolide (II), a crystalline precipitate began to deposit after several hours; this was shown to be the semicarbazone of dimethylbenzoylcarbinol (III). On reacting an aqueous sulfuric acid solution of 2,4-dinitrophenylhydrazine with the methyl lactolide, the 2,4-dinitrophenylhydrazone of dimethylbenzoylcarbinol was obtained. Formation from the methyl

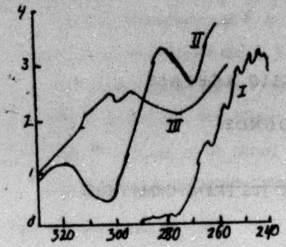


Fig. 1. I) Dimethylbenzoylcarbinol methyl lactolide; II) dimethylbenzoylcarbinol; III) methylphenylacetylcarbinol methyl ether.

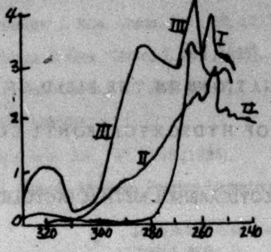
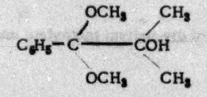


Fig. 2. I) Anhydrous dimethylbenzoylcarbinol dimer melting at 185-186°; II) ethylbenzoylcarbinolcyclodilactolide; III) dimethylbenzoylcarbinol oxalate ester.

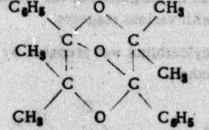
lactolide of carbonyl group derivatives, corresponding to ketoalcohols, indicates the ease of hydrolyzing the methyl lactolides under study in acid aqueous solutions.

In connection with this, we should note that the reaction between α-bromoisopropyl phenyl ketone and dry sodium methylate was performed by Aston, Clarke, Burgess, and Greenburg [2] in 1942. Based on the tendency of the substance to react with 2,4-dinitrophenylhydrazine with formation of a 2,4-dinitrophenylhydrazone, they incorrectly attributed to it the formula of dimethylbenzoylcarbinol methyl ether. They did not analyze the dinitrophenyl hydrazone for its methoxy group content; the ease of methyl lactolide hydrolysis led the American authors into error. According to physical constants and melting point, the 2,4-dinitrophenylhydrazone of their substance is identical with the one we prepared.

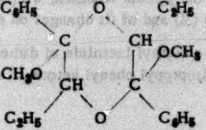
By reacting methyl alcohol with dimethylbenzoylcarbinol methyl lactolide, we obtained dimethylbenzoyl carbinol dimethylketal (IV); this was shown by hydrolyzing the substance obtained to the ketoalcohol, and identifying the latter.



(IV)



(V)



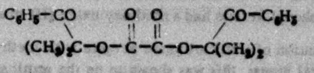
(VI)

By reacting 2% HCl in absolute methyl alcohol or benzene with the methyl lactolide, a substance is formed which melts at 184-185°, together with a small quantity of ketoalcohol; this was previously obtained by A.E. Favorsky and N. Mandryka from dimethylbenzoylcarbinol on storage [3]. The structure of this substance has not been shown. It is probable that it is an anhydrocyclodilactal, and has structure (V). Assumptions with regard to the presence of a dioxane ring in the compound and its bicyclic structure are based on similarity of the absorption spectrum of this substance (Fig. 2., curve I) with the absorption spectrum of ethylbenzoylcarbinol cyclodimethyldilactolide (VI) (Fig. 2, curve II), in which there is no doubt about the presence of dioxane rings [4].

Assumptions on forming the anhydrous form of the dioxydioxane by reacting sodium bisulfate with ketals of α-ketoalcohols were discussed by I. N. Nazarov [5].

On reacting the methyl lactolide with oxalic acid in benzene, the oxide ring is broken on the side of the two methyl groups, and the full oxalate ester of dimethylbenzoylcarbinol (VII) is formed, whose structure was confirmed by hydrolysis and identification of the hydrolysis products.

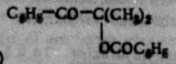
The ultraviolet absorption spectrum also indicates presence in the substance of a benzoyl grouping (maxima at λ = 322 mμ, at 284 mμ, and at 262 mμ) (Fig. 2, curve III).



$$(CH_3)_2C(COC_6H_5)-O-CO-CO-O-C(CH_3)_2(COC_6H_5)$$

(VII)

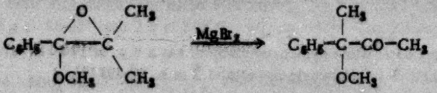
By reacting the methyl lactolide with benzoic acid in a benzene solution, the oxide ring is likewise readily opened, and a benzoic ester formed, evidently, of dimethylbenzoylcarbinol (VIII)


(VIII)

$C_6H_5-CO-C(CH_3)_2-OCOC_6H_5$

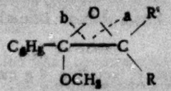
Conclusions on structure of this substance were drawn by analogy with oxalic acid esters where the ester structure was firmly established. Attempts to prepare the benzoic acid ester of dimethylbenzoylcarbinol by the usual method – by heating α-bromoisopropyl phenyl ketone with potassium benzoate in an alcohol solution – were unsuccessful; the bromoketone was recovered again in an unchanged form.

By comparing results of this study with data in the work by T. I. Temnikova and E. N. Kropacheva [6] on the relative action of acids on methyl lactolides (II) and (I), it can be seen that both methyl lactolides behave differently with regard to oxalic acid; whereas in reacting oxalic acid with dimethylbenzoylcarbinol methyl lactolide (II), ester formation occurs with oxide ring rupture on the side of the two methyl groups, in reacting oxalic acid with methylbenzoylcarbinol methyl lactolide, oxide ring rupture takes place on the phenyl side, and isomerization to phenylacetylcarbinol methyl ether was observed. We were able to cause isomeric transformation of dimethylbenzoylcarbinol methyl lactolide by action on it of magnesium bromide etherate in ether solution; here also oxide ring cleavage took place on the phenyl side with formation of methylphenylacetylcarbinol methyl ether:



The structure of the isomerization product was confirmed by oxidizing it with sodium hypobromite to methoxymethylphenylacetic acid, and also by spectrochemical methods. The absorption curve did not have a supplemental maximum in the λ region of 320 mμ, the maximum for the carbonyl group, as does phenylacetylcarbinol methyl ether, which shifts in the direction of longer waves (compare Fig. 1 of this work with Fig. 2 of reference [6]).

Thus, dimethylbenzoylcarbinol methyl lactolide is characterized by greater stability toward polymerization as compared with methylbenzoylcarbinol methyl lactolide, but shows a higher tendency toward oxide ring cleavage on hydrolysis and on reaction with various reagents; the order of this ring cleavage is the same – in forming esters of organic acids cleavage takes place on the side of the methyl groups (a); on action of sodium methylate and in isomerization, on the phenyl and methoxy group side (b):



where: R' and R = 2CH₃ or CH₃ and H.

EXPERIMENTAL

Preparation of dimethylbenzoylcarbinol methyl lactolide

A solution of 70 g bromoisopropylphenyl ketone in 100 ml absolute ether was added dropwise to a suspension of sodium methylate (from 10 g metallic Na) in 200 ml absolute ether with vigorous agitation. To obtain optimum yield (about 95%), the sodium methylate must be absolutely dry and finely pulverized. Reaction is completed in 7-10 hours. The ether solution was filtered from the mixture of NaBr and CH_3ONa; following distillation of the ether, the residue was distilled in vacuum. B.p. 85-85.5° at 9.5 mm, 75-75.5° at 5 mm.

d_4^{17} 1.0124; n_α^{17} 1.49259; n_D^{17} 1.49583; n_β^{17} 1.50633; MR_α 51.09; MR_β 52.29. $C_{11}H_{14}O_2\ulcorner$.
Calculated: MR_α 50.52; MR_β 51.65*

0.1247 g substance: 0.3375 g CO_2; 0.0894 g H_2O. 0.1208 g substance: 0.3274 g CO_2; 0.0872 g H_2O.
0.1923 g substance: 0.2510 g AgI. Found %: C 73.81, 73.91; H 8.02, 8.07; CH_3O 17.2.
$C_{11}H_{14}O_2$. Calculated %: C 74.16; H 7.90; OCH_3 17.4.

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* In calculating 0.35 was added per oxide ring increment for the α-line, and 0.45 for the β-line.

Reaction of the methyl lactolide with semicarbazide. A water-alcohol solution of semicarbazide acetate (from 1 g semicarbazide hydrochloride) was added to 1 g of the substance. The crystals separating in 24 hours were filtered and recrystallized from alcohol. M.p. 181-182°. The semicarbazone of dimethylbenzoylcarbinol melts at the same temperature. Mixture tests melted at the same temperature.

Reaction of the methyl lactolide with 2,4-dinitrophenylhydrazine. To 0.5 g of the substance dissolved in 20 ml alcohol was added a solution of 0.4 g dinitrophenylhydrazine and 2 ml H_2SO_4 in 3 ml water and 10 ml ethyl alcohol. The solution was allowed to stand overnight. The crystals which precipitated were separated, washed with alcohol, dried, and recrystallized from ligroin. M.p. 139-140°. The substance did not contain methoxy groups (determined by the Tseizel method).

0.1020 g substance: 14.4 ml N_2 (18°, 755.6 mm). 0.0859 g substance: 12.2 ml N_2 (18°, 755.3 mm). Found %: N 16.35, 16.44. $C_{16}H_{16}O_5N_4$. Calculated %: N 16.28.

Hydrolysis of the methyl lactolide. 5 g of the substance was heated on a boiling water bath with vigorous agitation for a 6 hour period with 100 ml of aqueous 5% sulfuric acid. On cooling, the oil was extracted with ether, dried with $MgSO_4$, and the hydrolysis products distilled.

B.p. 128-129° at 12 mm; semicarbazone, m.p. 181-182°.

Found %: N 18.8. $C_{11}H_{15}O_2N_3$. Calculated %: N 19.01.

A glycol was obtained by reaction with magnesium phenyl bromide: 2-methyl-1,1-diphenylpropandiol-1,2 with a m.p. of 88-89°.

According to literature data, dimethylbenzoylcarbinol has a b.p. of 115-116° at 7 mm; semicarbazone m.p. 188° [7], 177-178° [8]; 2-methyl-1,1-diphenylpropandiol-1,2 m.p. 88-89° [9].

Reaction of dimethylbenzoylcarbinol methyl lactolide with methyl alcohol. 5 g of the methyl lactolide was dissolved in 50 ml methyl alcohol and allowed to stand for two days. After distilling the methyl alcohol under vacuum, an oily substance and crystals remained. The liquid portion was shown to be a mixture of substances. The crystals after recrystallization from light petroleum ether melted at 54-55° Yield 1 g.

0.1195 g substance: 0.2997 g CO_2; 0.0932 g H_2O. 0.1036 g substance: 0.2595 g CO_2; 0.0816 g H_2O. Methoxyl determination according to Fibek: 0.0436 g substance: 24.7 ml 0.1 N $Na_2S_2O_3$. 0.0395 g substance: 22.5 ml 0.1 N $Na_2S_2O_3$. 0.1136 g substance: 11.9 ml CH_4 (13°, 756 mm). 0.1025 g substance: 10.8 ml CH_4 (13°, 756 mm). Found %: C 68.43, 68.36; H 8.73, 8.81; OCH_3 29.36, 29.45; number of active hydrogens 0.96, 0.97. $C_{12}H_{18}O_3$. Calculated %: C 68.57; H 8.57; OCH_3 29.52; number of active hydrogens 1.

Hydrolysis of the substance obtained, which appeared to be a ketal of dimethylbenzoylcarbinol, was performed by heating it on a water bath with 5% H_2SO_4 in water for a 1 hour period. Dimethylbenzoylcarbinol was identified as its semicarbazone with a m.p. of 181-182°.

Action of 1% HCl in benzene on dimethylbenzoylcarbinol methyl lactolide 4 g methyl lactolide was added dropwise to 50 ml dry benzene containing 1% HCl. The reaction takes place with warming. After 12 hours, the benzene solution was washed with water and soda solution and dried with $MgSO_4$. After removing the benzene in a vacuum, an oil was obtained which gave a positive reaction for halogens and contained dimethylbenzoylcarbinol. The crystalline substance was recrystallized from a mixture of alcohol and benzene; m.p. 185-186°. Found %: C77.37; H 7.11. $C_{20}H_{22}O_3$. Calculated %: C 77.40; H 7.09

From the action of 1% HCl in absolute methyl alcohol there was similarly obtained dimethylbenzoylcarbinol and the substance with a 185-186° m.p.

Reaction of dimethylbenzoylcarbinol methyl lactolide with oxalic acid in benzene solution. 10 g methyl lactolide was added dropwise to 2 g anhydrous oxalic acid suspended in 34 ml dry benzene. The reaction mixture was allowed to stand for 24 hours, during the course of which the oxalic acid gradually went into solution. On the next day, the benzene solution was washed with an aqueous soda solution and dried over $MgSO_4$. After distilling the benzene under vacuum, a yellow liquid and colorless crystals remained as a residue. The crystals were separated from the liquid by filtration. The crystals were recrystallized from ethanol; m.p. 136°. (5 g).

0.1096 g substance: 0.2790 g CO_2; 0.0554 g H_2O. 0.1141 g substance: 0.2902 g CO_2; 0.0591 g H_2O. The substance did not contain either OH or OCH_3 groups. Found %: C 69.43, 69.36; H 5.66, 5.80. $C_{22}H_{22}O_6$. Calculated %: C 69.11; H 5.76.

Hydrolysis of the oxalate ester was performed by heating with aqueous alcoholic potassium hydroxide solution for a 5 hour period on a water bath. The ethyl alcohol was distilled under vacuum and the residue subjected to ether extraction. Dimethylbenzoylcarbinol was separated from the neutral products, identified by its absorption spectrum in the ultraviolet and by its semicarbazone, which melted at 180-181°. No depression of melting point was observed with the semicarbazone of dimethylbenzoylcarbinol. Oxalic acid was separated via its calcium salt and acidification. After two recrystallizations from water and drying, the acid had m.p. 189° in a sealed capillary. The melting point of a mixture with commercial oxalic acid was the same. The calcium salt was prepared.

Reaction of dimethylbenzoylcarbinol methyl lactolide with benzoic acid. 3 g of the methyl lactolide was added to 3 g benzoic acid dissolved in 50 ml benzene. The solution was allowed to stand overnight, and then washed with an aqueous soda solution and dried over $MgSO_4$. After distilling the benzene, colorless crystals remained, which after two recrystallizations from light petroleum ether melted at 61.5-62.5°.

0.1037 g substance: 0.2885 g CO_2; 0.0535 g H_2O. 0.1123 g substance: 0.3138 g CO_2; 0.0607 g H_2O. Found %: C 75.93, 76.22; H 5.74 6.05. $C_{17}H_{16}O_3$. Calculated %: C 76.12; H 5.97.

Isomerization of dimethylbenzoylcarbinol methyl lactolide into methylphenylacetylcarbinol methyl ether. Isomerization was conducted with magnesium bromide etherate, prepared according to B. N. Menshutkin [10]. 7 g bromine was added to 1.5 g Mg under a layer of 10 ml absolute ether with strong agitation and cooling; the solution was then heated. After a little while two layers appeared in the flask: the upper one of ether and the lower one, an ether complex of magnesium bromide. 5 g dimethylbenzoylcarbinol methyl lactolide was then added dropwise to the flask and the solution agitated for a 5 hour period. The ether solution was washed with dilute hydrochloric acid and then with alkali, and dried with $MgSO_4$. As a result of distillation at 3 mm, two fractions were obtained; 2.5 g at 85-86°, and 2 g at 86-89°. After a second distillation a narrow fraction was separated boiling at 86-86.5° at 3 mm.

d_4^{15} 1.037; n_α^{15} 1.49694. MR_α 50.34. $C_{11}H_{14}O_2\overline{F}_3$. Calculated MR_α 50.63.

0.1234 g substance: 0.3340 g CO_2; 0.0906 g H_2O. 0.1258 g substance: 0.3415 g CO_2; 0.0883 g H_2O. 0.0437 g substance: 14.35 ml 0.1 N $Na_2S_2O_3$. Found %: C 73.81, 74.05; H 8.22, 7.86; OCH_3 16.98. $C_{11}H_{14}O_2$ Calculated %: C 74.16; H 7.90; OCH_3 17.40.

The semicarbazone was obtained by the usual method. After recrystallization from alcohol it melted at 154°.

0.1023 g substance: 15.3 ml N_2 (15°, 733 mm). 0.0983 g substance: 14.9 ml N_2 (16°, 733 mm). Found %: N 18.01, 18.21. $C_{12}H_{17}O_2N_3$. Calculated %: N 17.87.

Methoxyketone oxidation. Oxidation was performed by sodium hypobromite prepared from 2.7 g of NaOH and 4 g bromine. 1.5 g ketone was added dropwise to the hypobromite solution at 20° with constant agitation; heavy droplets began to collect at the bottom of the flask after 30 minutes. Reaction continued for 3 hours. Bromoform was separated and was distilled after drying. B.p. 151-152°; n_D^{17} 1.609 (according to the literature data, b.p. 150.5°, n_D^{19} 1.598.

The alkaline solution was extracted with ether to remove neutral products, and then dried and acidified with hydrochloric acid. The oil separated was extracted with ether and dried over $MgSO_4$. The acid was precipitated as its ammonium salt from the ether solution, using dry NH_3. The ammonium salt was a white colored crystalline solid, soluble in water; by reacting it with $AgNO_3$ solution, the silver salt of the acid was separated; this was used for analysis.

0.1410 g substance: 0.2150 g CO_2; 0.0515 g H_2O. 0.0530 g Ag. 0.1462 g substance: 0.2252 g CO_2; 0.0530 g H_2O; 0.0551 g Ag. 0.0786 g substance: 15.7 ml 0.1 N $Na_2S_2O_3$. Found %: C 41.60, 41.99. H 4.09, 4.05; Ag 37.61, 37.70; OCH_3 10.33. $C_{10}H_{11}O_3Ag$. Calculated %: C 41.81; H 3.83; Ag 37.63; OCH_3 10.80.

SUMMARY

1. Dimethylbenzoylcarbinol methyl lactolide (1-methoxy-1-phenyl-2,2-dimethylethylene oxide) is obtained by reacting sodium methylate in absolute ether with α-bromoisopropyl phenyl ketone. The methyl lactolide was stable and did not polymerize on storage, but was readily hydrolyzed in aqueous acid solutions with formation of dimethylbenzoylcarbinol; because of this the corresponding ketoalcohol derivative was obtained on reacting the methyl lactolide with semicarbazide or 2,4-dinitrophenylhydrazine.

2. The dimethylketal of dimethylbenzoylcarbinol is formed by reacting the methyl lactolide with methyl alcohol.

3. On reacting the methyl lactolide with benzoic or oxalic acids, corresponding esters of dimethylbenzoyl carbinol are formed.

4. Under action of magnesium bromide etherate, the methyl lactolide undergoes isomerization and methylphenylacetylcarbinol methyl ether is obtained.

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THE PROBLEM OF FORMING DERIVATIVES OF β-IMINODIACRYLIC ACIDS

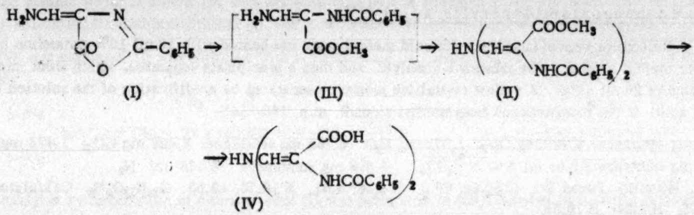
I. T. Strukov

In studying chemical properties of certain α-substituted β-aminoacrylic acids, it was found that they could be rather readily transformed into derivatives of β-aminodiacrylic acids.

A similar reaction was described by M. V. Rubtsov [1]. By heating the ethyl ester of β-p-anisidineacrylic acid in a vacuum at 100°, M. V. Rubtsov obtained the ethyl ester of β-p-anisidinediacrylic acid and p-anisidine.

The author has shown [2] that in ether solution in presence of hydrogen chloride the methyl ester of α-phenyl-β-aminoacrylic acid changes to the methyl ester of β-iminodi-(α-phenylacrylic acid). On saponifying the ester with an alcoholic potassium hydroxide solution, the potassium salt of β-iminodi-(α-phenylacrylic acid) was obtained, and the free acid prepared from it.

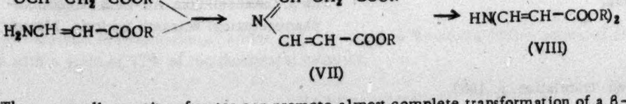
In the present paper we describe another similar transformation reaction. By action of a hydrogen chloride solution in methyl alcohol on 4-aminomethylene-2-phenyl-5-oxazolone (I), the methyl ester of β-iminodi-(α-benzoylaminoacrylic acid) (II) slowly forms. Evidently, the reaction is via a stage of forming the methyl ester of α-benzoylamido-β-aminoacrylic acid (III). By saponifying ester (II) with potassium hydroxide solution, the potassium salt of the acid was formed, and then the free β-iminodi-(α-benzoylamidoacrylic acid) (IV):



To explain the reaction mechanism, it is necessary to make several very probable assumptions. Esters of β-aminoacrylic acid exist in two tautomeric forms (V) and (VI):

$$\underset{\text{(V)}}{H_2N{-}CH{=}CH{-}COOR} \rightleftarrows \underset{\text{(VI)}}{HN{=}CH{-}CH_2{-}COOR.}$$

The presence of hydrogen chloride will promote transformation of the β-aminoacrylic acid ester (V) into the aldimine form (VI), and presence of traces of water, always present in alcohol or ether, leads to decomposition of the molecule into ammonium chloride and a β-oxopropionic acid ester. Subsequently, the β-oxopropionic acid ester enters into reaction with an as-yet-unchanged molecule of β-aminoacrylic acid ester; here the water separated takes up hydrogen chloride, and the tautomeric form (VII) is obtained, which changes into a β-iminodiacrylic acid ester (VIII):



Thus, a small quantity of water can promote almost complete transformation of a β-aminoacrylic acid ester into a β-iminodiacrylic acid ester. This was shown by transforming (I) into (II); the yield of β-iminodi-(α-benzoylamidoacrylic acid) methyl ester reached 90%.

In presence of hydrogen chloride, this reaction goes without consumption of external energy, while heating is necessary to convert the ethyl ester of β-p-anisidineacrylic acid into the ethyl ester of β-p-anisidinediacrylic acid.

We may assume that formation of β-iminodiacrylic acid esters and their derivatives takes place by a scheme which may be considered as a general one for the given series of compounds.

EXPERIMENTAL

β-Iminodi-(α-phenylacrylic acid)

1 g β-iminodi-(α-phenylacrylic acid) methyl ester was heated with 10 ml 10% potassium hydroxide solution in methyl alcohol for a 24 hour period at 50-55°. The white crystalline precipitate which separated was filtered, washed with methyl alcohol, and dissolved in 50 ml water. The solution was treated with 0.5 g charcoal at 15-20° and filtered. On acidification of the filtrate, a pale yellow substance separated which, after recrystallization from methyl alcohol, melted at 168-170° (with decomposition).

7,374 mg substance: 0.300 ml N_2 (21°, 721 mm). 7.673 mg substance: 0.307 ml N_2 (21°, 721 mm). 0.0206 g substance: 1.31 ml 0.1 N NaOH. Found %: N 4.48, 4.46; COOH 28.59. $C_{18}H_{15}O_4N$. Calculated %: N 4.53; COOH 29.12.

Methyl ester of β-iminodi-(α-benzoylamidoacrylic acid) (II)

25 ml methyl alcohol was saturated with 5 g dry hydrogen chloride. 4 g 4-aminomethylene-2-phenyl-5-oxazolone was added to the solution and allowed to stand for 5 days at 18-20°. The azlactone gradually went into solution. and a crystalline precipitate simultaneously separated in the form of long, pale-yellow, silky needles. The residue was filtered (4 g) and recrystallized from methyl alcohol. M.p. 230-231° (with decomposition).

4.945 mg substance: 0.466 ml N_2 (25°, 737.5 mm). 4.115 mg substance: 0.373 ml N_2 (23°, 739 mm). 5.692 mg substance: 8.31 ml 0.02 N $Na_2S_2O_3$. 5.097 mg substance: 7.39 ml 0.02 N $Na_2S_2O_3$. Found %: N 10.02, 10.16; OCH_3 15.09, 15.00. $C_{22}H_{21}O_6N_3$. Calculated %: N 9.95; OCH_3 14.62.

β-Iminodi-(α-benzoylamidoacrylic acid) (IV)

1 g of β-iminodi-(α-benzoylamidoacrylic acid methyl ester was heated with 10 ml 10% potassium hydroxide solution in methyl alcohol. The substance dissolved and then a precipitate separated, which went into solution on addition of 20 ml water. A yellow crystalline substance separated on acidification of the solution with hydrochloric acid. It was recrystallized from methyl alcohol, m.p. 165-166°.

3.116 mg substance: 6.929 mg CO_2; 1.271 mg H_2O. 3.768 mg substance: 8.422 mg CO_2; 1.428 mg H_2O. 4.701 mg substance: 3.61 ml 0.01 N H_2SO_4. 5.898 mg substance: 6.538 ml N_2 (23.5°, 749 mm). Found %: C 60.68, 60.0. H 4.56, 4.41. N 10.75, 10.53. $C_{20}H_{17}O_6N_3$. Calculated %: C 60.78; H 4.34; N 10.63.

SUMMARY

1. The transformation of β-amino-α-benzoylamidoacrylic acid methyl ester into β-iminodi-(α-benzoylamidoacrylic acid) methyl ester is shown.

2. Assumptions are discussed with regard to reaction mechanism for forming esters of β-iminodiacrylic acids and their derivatives from the corresponding β-aminoacrylic acid esters.

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* See Consultants Bureau Translation, p. 1657.

SYNTHESIS AND TRANSFORMATION OF β-(DIETHYLAMINO) ETHYLMETHYLVINYLETHINYLCARBINOL

A. G. Terzyan

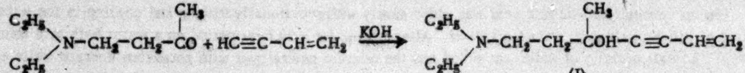
The condensation of carbonyl compounds with singly substituted acetylenic hydrocarbons, discovered and studied by A. E. Favorsky [1], has had wide application as a most general method for preparing acetylenic alcohols and glycols. This reaction (in its various variations) continues to have wide development even at the present time. In particular, I. N. Nazarov and his coworkers have studied in detail the reaction of condensing acetylenic hydrocarbons with aminoketones of the piperidine series [2].

The similar condensation of vinylacetylene or its homologs with aliphatic aminoketones has not been reported previously.

It was shown in a previous paper [3] that on condensing vinylacetylene with β-dimethylaminobutanone in presence of powdered potassium hydroxide, aminoalcohols of the vinylacetylene series are formed, from which saturated and unsaturated amines, as well as the corresponding aminoalcohols, were obtained by dehydration and catalytic hydrogenation.

The present paper is concerned with synthesis of a second example of this aminoalcohol series – β-(diethylamino)-ethylmethylvinylethinylcarbinol (I), and also to describe the products of its corresponding transformations.

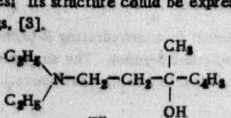
The aminoalcohol (I) was obtained with a 70.9% yield by condensing vinylacetylene with β-diethylaminobutanone:



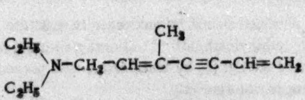
(I)

Catalytic hydrogenation of aminoalcohol (I) was performed in ethyl alcohol in presence of platinum black. The corresponding saturated aminoalcohol – 1-diethylamino-3-methylheptanol-3 (II) – was obtained with a 73% yield.

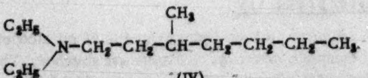
By dehydrating the starting aminoalcohol (I) with sulfuric acid, we obtained an amine of the divinylacetylene series; its structure could be expressed by formula (III) by analogy with previously prepared and studied homologs. [3].



(II)



(III)



(IV)

By catalytic hydrogenation of amine (III), we obtained the corresponding saturated amine (IV), which was formed with a yield of 77% of the theoretical quantity.

EXPERIMENTAL

β-(Diethylamino)ethylmethylvinylethinylcarbinol (I)

A solution of 21.3 g of β-diethylaminobutanone and 20 ml vinylacetylene in 25 ml dry ether was added in small portions with continued shaking and cooling in an ice-salt mixture during a 4 hour period to a mixture of 12 g powdered potassium hydroxide in 40 ml dry ether. The reaction mixture was stirred for 4 hours with cooling in ice water, and for 3 hours at room temperature. On the following day, the ethereal solution of reaction products was washed with water and dried over sodium sulfate. After removing the ether, the residue was vacuum distilled. 20.6 g (70.91% of the theoretical quantity) of a colorless oily substance was obtained, with b.p. 123-125° at 22 mm.

d_4^{20} 0.9020; n_D^{20} 1.4800; found: MR_D 61.53. $C_{12}H_{21}ON$. Calculated MR_D 60.73.

0.1022 g substance: 0.2762 g CO_2; 0.1016 g H_2O. Found %: C 73.70; H 11.04. $C_{12}H_{21}ON$. Calculated %: C 73.84; H 10.76. 0.0658 g substance: 6.6 ml 0.05 N H_2SO_4. 0.0586 g substance: 6.99 ml 0.05 N H_2SO_4. Found: M 199,195.1. $C_{12}H_{21}ON$. Calculated: M 195. 0.0636 g substance: 12.8 ml CH_4 (26.5°, 678 mm). 0.0586 g substance: 12.0 ml CH_4(31°, 674 mm). Found OH groups: 1. $C_{12}H_{21}ON$. Calculated OH groups: 1.

1-Diethylamino-3-methylheptanol-3 (II).

6.65 g freshly distilled carbinol (I) was hydrogenated in 20 ml ethyl alcohol with platinum black. Hydrogenation was rapid at first, and slowed down at the end. 2.29 liters of hydrogen is required for complete reduction; 2.27 liters was absorbed. 5.03 g (73.51% of the theoretical quantity) of 1-diethylamino-3-methylheptanol-3 (II) was obtained, with b.p. 108° at 20 mm; a mobile liquid with a specific amine odor.

d_4^{20} 0.8562; n_D^{20} 1.4487; found: MR_D 62.87. $C_{12}H_{27}ON$. Calculated MR_D 63.20.

0.0936 g substance: 4.7 ml 0.1 N H_2SO_4. Found: M 198.2. $C_{12}H_{27}ON$. Calculated M 201.
0.0938 g substance: 0.2472 g CO_2; 0.1264 g H_2O. Found %: C 71.87; H 13.78. $C_{12}H_{27}ON$. Calculated %: C 71.64; H 13.43. 0.0640 g substance: 17 ml CH_4 (22°, 680 mm). Found: OH groups: 1. $C_{12}H_{27}ON$. Calculated OH groups: 1.

Its hydrogen chloride salt, obtained by passing a stream of dry hydrogen chloride through an ether solution of the amine, was a hygroscopic amorphous white powder, which came out as a viscous, non-crystallizing mass on attempts to crystallize it.

0.1103 g substance: 0.0686 g AgCl. Found %: Cl 15.39. $C_{12}H_{28}ONCl$. Calculated %: Cl 14.95.

1-Diethylamino-3-methylheptadiene-2,6-yne-4 (III).

138 ml concentrated sulfuric acid was added slowly while continually stirring and cooling in ice water to a mixture of 115 g carbinol (I) and 64 ml water. After stirring for a 20 hour period on a water bath at a temperature of 60-70°, a small quantity of water was added and the mixture neutralized with potassium acetate while cooling with ice. After removing the ether layer, the water layer was washed with ether; the ether solution was dried with sodium sulfate and the solvent distilled. On distilling the remaining oil 78 g (74.71% of the theoretical quantity) of a pale yellow liquid was obtained, having an amine odor, and boiling at 91-92° at 9 mm.

d_4^{20} 0.8896; n_D^{20} 1.5058; found MR_D 59.47. $C_{12}H_{19}N$. Calculated MR_D 58.62.

0.0308 g substance: 3.36 ml 0.05 N H_2SO_4. Found M 179.1. $C_{12}H_{19}N$. Calculated: M 177. 0.0865 g substance: 7.2 ml N_2 (24°, 679 mm). Found %: N 8.19. $C_{12}H_{19}N$. Calculated %: N 7.91.

The compound obtained should be analogous in structure with the product from dehydrating β-(dimethylamino)ethylmethylvinylethinylcarbinol – 1-dimethylamino-3-methyl-heptadiene-2,6-yne-4. The structure of this substance was established earlier [3] by oxidizing it with potassium permanganate to dimethylaminoacetic acid, identified via its hydrogen chloride salt.

1-Diethylamino-3-methylheptane (IV)

2.7 g freshly distilled aminodienyne (III) was hydrogenated in 20 ml alcohol over a platinum catalyst. 1.36 liters of hydrogen is required for complete reduction; 1.3 liters was absorbed. The catalyst was filtered, alcohol distilled, and the product distilled under vacuum. 2.2 g amine (IV) (77.3% of the theoretical quantity) was obtained as a mobile liquid, boiling at 80-82° at 11 mm.

d_4^{20} 0.8172; n_D^{20} 1.4610; found: MR_D 62.11. $C_{12}H_{27}N$. Calculated: MR_D 61.56.

0.0472 g substance: 2.6 ml 0.1 N H_2SO_4. Found: M 181.7. $C_{12}H_{27}N$. Calculated M: 185.
0.1304 g substance: 9.4 ml N_2 (23°, 680 mm). Found %: N 7.43. $C_{12}H_{27}N$. Calculated %: N 7.56.

The hydrogen chloride salt of this amine was a hygroscopic, amorphous, white powder, which decomposed on storage in air, and came out in the form of a viscous noncrystallizing mass on attempts to recrystallize it.

SUMMARY

1. It was shown that β-(diethylamino)ethylmethylvinylethinylcarbinol, obtained by condensing β-diethylaminobutanone with vinylacetylene, forms the corresponding saturated carbinol on catalytic hydrogenation.

2. By reacting with sulfuric acid, β-(diethylamino)ethyl-methylvinylethinylcarbinol is dehydrated to the corresponding aminodienyne. The corresponding aminoheptane is obtained by hydrogenation of the latter.

3. The following were obtained for the first time and described: β-(diethylamino)ethylmethylvinylethinylcarbinol, 1-diethylamino-3-methylheptadiene-2,6-yne-4, 1-diethylamino-3-methylheptanol-3, and 1-diethylamino-3-methylheptane.

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RESEARCH IN THE FIELD OF ALKANOSULFONIC ACIDS

X. METHYLATION OF THE N-ARYLAMIDES OF ALKANOSULFONIC ACIDS

A. G. Kostsova

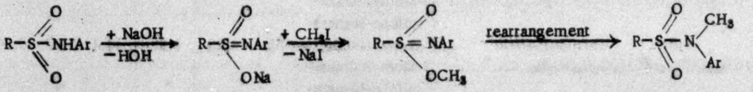
N-Arylamides of alkanosulfonic acids, having the general formula RSO_2NHAr, contain in their composition the NH group with a mobile hydrogen atom, which can be replaced by various radicals, for example, alkyl, acyl, and others. Nevertheless, the alkylation and acylation reactions of the N-arylamides of alkanosulfonic acids have been studied very little [1]. The reactions mentioned have been described with relative completeness in the literature only for the p-phenetidide of ethanesulfonic acid [2]. Directions for alkylation of N-arylamides of disulfonic acids are present in the literature [3, 4].

Alkylation is usually carried out in an alkaline medium, with alkyl halides, alkyl sulfates, diazomethane, and other reagents playing the role of alkylating agents.

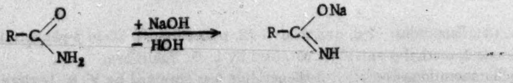
The purpose of the present work was to study the methylation of anilides, p-anisidides, and certain p-phenetidides of alkanosulfonic acids synthesized by the author. The author used methyl iodide as the methylating agent. Methylation was carried out in an alkaline medium. The methylation products separated readily from the reaction mixture, due to complete insolubility in alkali. This property readily distinguishes them from the initial N-arylsulfonamide, which, in contrast, dissolves readily in alkalies. Attempts to carry out methylation without alkalies, in the presence of absolute ether medium, as well as in the absence of solvent, by direct interaction of N-arylsulfonamides with methyl iodide, led to negative results. In both cases unchanged N-arylsulfonamides were isolated.

These experiments indicated that methylation of the latter proceeds under strictly defined conditions, notably, only in an alkaline medium. On the other hand, the point should be stressed that N-arylsulfonamides, as the author's observations have shown, possess a neutral character; this is demonstrated by the neutral reaction to litmus, and also by the pH value, which fluctuates from 6 to 7.

However, as neutral compounds they dissolve readily in alkalies, in a manner analogous to primary and secondary nitro compounds, i.e., they behave as typical pseudo acids. Hence, proceeding from the fact that N-arylsulfonamides do not alkylate without alkalies, the author advances the assumption that they isomerize to the aci-form under the action of alkalies, and in this form they methylate, the resulting O-methyl derivative then regrouping into the N-methyl derivative according to the following equation:



Such an isomerization is possible, considering also the analogy to amides of the carboxylic acids, which are inclined toward similar tautomeric transformations. Therefore, for some of their metallic derivatives, a structure can be attributed, corresponding to the tautomeric form



The methylated N-arylamides of the alkanosulfonic acids obtained by the author were colorless, crystalline substances, readily soluble in alcohol, insoluble in ether, and stable to water hydrolysis; for example, they remained unchanged after 10 hours of boiling with water.

EXPERIMENTAL

The anilides, p-anisidides, and p-phenetidides required for methylation were synthesized by the method described in the preceding works [5] of the author. 7-8% alkali was used to dissolve the N-arylsulfonamides. Methyl iodide was taken in four times the amount calculated according to the equation. Methylation procedure

No.	Formula	Name	M.p. (°C)	Quantity of initial substance taken (g)		Yield of product (%)	Analytical data for N (%)		Empirical formula
				N-arylsulfonamide*	Methyl iodide		Found	Calc.	
1	$CH_3SO_2N(CH_3)C_6H_5$	Methanesulfono-N-methylanilide	78*	0.6	2.0	59	7.48	7.57	$C_8H_{11}O_2NS$
2	$CH_3CH_2SO_2N(CH_3)C_6H_5$	Ethanesulfono-N-methylanilide	65	0.5	1.5	40	7.06	7.03	$C_9H_{13}O_2NS$
3	$(CH_3)_2CHSO_2N(CH_3)C_6H_5$	2-Methylethanesulfono-N-methylanilide	55	0.4	1.12	38	6.52	6.57	$C_{10}H_{15}O_2NS$
4	$CH_3CH_2CH_2CH_2SO_2N(CH_3)C_6H_5$	Butanesulfono-N-methylanilide	54	1.8	5.2	62.5	6.13	6.16	$C_{11}H_{17}O_2NS$
5	$(CH_3)_2CHCH_2SO_2N(CH_3)C_6H_5$	2-Methylpropanesulfono-N-methylanilide	72	0.5	1.3	34	6.07	6.16	$C_{11}H_{17}O_2NS$
6	$(CH_3)_2CHCH_2CH_2SO_2N(CH_3)C_6H_5$	2-Methylbutanesulfono-N-methylanilide	81	0.35	0.80	40	5.57	5.80	$C_{12}H_{19}O_2NS$
7	$CH_3SO_2N(CH_3)C_6H_4OCH_3$	Methanesulfono-N-methyl-p-anisidide	69	0.6	1.78	36	6.42	6.51	$C_9H_{13}O_3NS$
8	$CH_3CH_2SO_2N(CH_3)C_6H_4OCH_3$	Ethanesulfono-N-methyl-p-anisidide	20(?)	0.4	1.0	–	–	–	$C_{10}H_{15}O_3NS$
9	$(CH_3)_2CHSO_2N(CH_3)C_6H_4OCH_3$	2-Methylethanesulfono-N-methyl-p-anisidide	56	0.35	0.80	43.2	5.72	5.76	$C_{11}H_{17}O_3NS$
10	$CH_3CH_2CH_2CH_2SO_2N(CH_3)C_6H_4OCH_3$**	Butanesulfono-N-methyl-p-anisidide	45	0.31	0.8	78.7	5.10	5.44	$C_{12}H_{19}O_3NS$
11	$(CH_3)_2CHCH_2SO_2N(CH_3)C_6H_4OCH_3$	2-Methylpropanesulfono-N-methyl-p-anisidide	53	0.6	0.7	35	5.30	5.44	$C_{12}H_{19}O_3NS$
12	$(CH_3)_2CHCH_2CH_2SO_2N(CH_3)C_6H_4OCH_3$	2-Methylbutanesulfono-N-methyl-p-anisidide	55	0.35	0.8	44.4	5.06	5.16	$C_{13}H_{21}O_3NS$
13	$(CH_3)_2CHSO_2N(CH_3)C_6H_4OC_2H_5$	2-Methylethanesulfono-N-methyl-p-phenetidide	56	0.4	0.9	47.6	5.22	5.44	$C_{12}H_{19}O_3NS$
14	$(CH_3)_2CHCH_2CH_2SO_2N(CH_3)C_6H_4OC_2H_5$***	2-Methylbutanesulfono-N-methyl-p-phenetidide	65	0.4	0.8	71.4	4.51	4.91	$C_{14}H_{23}O_3NS$

* Initial N-arylsulfonamides: 1-6, anilides; 7-12, p-anisidides; 13-14 p-phenetidides.

** Butanesulfono-N-methyl-p-anisidide obtained by L. D. Yakimova.

*** 2-Methylbutanesulfono-N-methyl-p-phenetidide was obtained by V. D. Levitan

used by the author was the same for all of the N-arylsulfonamides; a general description is therefore given below, and specific data are given in the table only for the most characteristic experiments. Melting points for the synthesized methylated derivatives are also placed in the table.

The requisite quantity of N-arylsulfonamide was dissolved in a small volume of alkali (3-4 ml). A four-fold excess of methyl iodide was added to the alkaline solution, the mixture shaken vigorously, and the emulsion formed heated on a water bath at 40-45° with a reflux condenser for 1-1.5 hours. After termination of heating, the mixture was left at room temperature until the following day. The contents of the reaction flask were then poured out onto a large watch glass or into a crystallizing dish for evaporation of the excess methyl iodide. As the latter evaporated, colorless crystals separated from the alkaline solution, which were separated from the alkalies, washed with water, dried and then recrystallized from a mixture of alcohol and water.

Upon methylating ethanesulfono-p-anisidide, the reaction product separated from alkaline solution as an oil, which did not crystallize upon cooling, or upon prolonged rubbing with a glass rod. In such case the oil was carefully separated from the alkali, dissolved in a small amount of alcohol, and precipitated with water by cooling and rubbing with a glass rod. Crystals were isolated from the water-alcohol mixture, which softened at 9-10°. Attempt to separate by filtration resulted in conversion to an oily spot on the filter. Nevertheless, it was possible to isolate a very small amount of the crystals. The melting point was about 20°. It was not possible to analyze the product.

SUMMARY

1. The methylation reaction for the anilides, p-anisidides and p-phenetidides of alkane sulfonic acids has been studied.

2. The N-methylanilides and N-methyl-p-anisidides of methane-, ethane-, 2-methylethane-, butane-, 2-methylpropane- and 2-methylbutane-sulfonic acids, and the N-methyl-p-phenetidides of 2-methylethane and 2-methylbutane sulfonic acids have been synthesized and characterized for the first time

3. It has been demonstrated that methylation proceeds only in an alkaline medium. Methylation does not proceed in absolute ether or in the absence of solvent.

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* See Consultants Bureau Translation, p. 1471.

ORGANIC INSECTOFUNGICIDES

XIV. SYNTHESIS OF MIXED ESTERS OF DITHIOPHOSPHORIC ACID

N. N. Melnikov and K. D. Shvetsova-Shilovskaya

Mixed esters of phosphoric and thiophosphoric acids have acquired greater and greater importance in agriculture as a resource in the struggle against various plant pests, and their scale of application is continnuously increasing [1-7]. A favorable property of this class of compounds is their rather universal character and rapidity of action upon various plant pests. Of interest in this respect are the esters of dithiophosphoric acid, which although somewhat less active than the mixed esters of thiophosphoric acid, are less dangerous to work with [8].

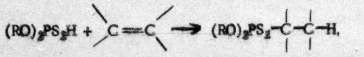
There are described in the literature only a limited number of methods for the synthesis of dithiophosphoric acid esters, the most important among them being the reaction of dialkyldithiophosphoric acid salts with halogen derivatives [9, 10].

$$(RO)_2PSSNa + R'X \rightarrow (RO)_2PSSR'. \qquad (1)$$

By this method has been obtained a majority of the mixed esters of dithiophosphoric acid described up to the present time. However, this method produces good ester yields only in those cases where the halogen of the halogen derivatives is sufficiently mobile.

It was of interest to the authors to study the addition reaction of dialkyldithiophosphoric acid to the double bond of unsaturated compounds, and to clarify the possibility of synthesizing mixed esters of dithiophosphoric acid by such reaction. The addition of dialkylphosphorous acids to unsaturated compounds was achieved recently by A. N. Pudovik and B. A. Arbuzov [11-15].

As a result of experiments carried out at the start of 1951, it was possible to determine that the reaction of dialkyldithiophosphoric acid with unsaturated compounds will proceed according to the following scheme:



$$(RO)_2PS_2H + \rangle C{=}C\langle \rightarrow (RO)_2PS_2{-}\overset{|}{\underset{|}{C}}{-}\overset{|}{\underset{|}{C}}{-}H, \qquad (2)$$

as the result of which quite satisfactory yields of dithiophosphoric acid esters have been produced. The reaction proceeds in the cold in the presence of small amounts of solid potassium hydroxide or other bases. The reaction of dialkyldithiophosphoric acid with unsaturated hydrocarbons proceeds according to the following general equation:

$$(RO)_2PSSH + CH_2{=}CHR' \rightarrow (RO)_2PSSCH_2CH_2R'. \qquad (3)$$

This reaction has been studied by the authors, using as an example the interaction of dialkyldithiophosphoric acids with styrene. The resulting compounds and their properties are given in Table 1.

It should be mentioned that after completion of the given work, there appeared directions in the literature for the synthesis of certain of the compounds [16] given in Table 1.

The interaction of dialkyldithiophosphoric acids with unsaturated compounds or with esters of the unsaturated alcohols proceeds according to scheme (4):

$$(RO)_2PSSH + CH_2{=}CHOCOCH_3 \rightarrow (RO)_2PSSCH_2{-}CH_2OCOCH_3 \qquad (4)$$

In this fashion allyl alcohol and vinyl acetate reacted. The compounds synthesized by the authors, and their properties, are given in Table 2.

The reaction of dialkyldithiophosphoric acids with unsaturated monobasic acids proceeds analogously (Scheme 5):

$$(RO)_2PSSH + CH_2{=}CHCOOR' \rightarrow (RO)_2PSSCH_2CH_2COOR'. \qquad (5)$$

The compounds synthesized and their properties are given in Table 3.

TABLE 1

Mixed Esters of Dithiophosphoric Acid Obtained from Alcohols and Dialkyldithiophosphoric Acids

Initial compound		Yield	Boiling point (°)	Pressure (in mm)	n_D^{20}	d_4^{20}	Phosphorus analysis	
							P calc'd (%)	P found (%)
$(CH_3O)_2PS_2H$	$CH_2{=}CH{-}C_6H_5$	50	128-132	0.45	1.5705	1.2108	11.82	11.5/11.65
$(C_2H_5O)_2PS_2H$	$CH_2{=}CH{-}C_6H_5$	35	135-137	0.15	1.5498	1.1444	10.67	11.0/11.28
$(C_3H_7O)_2PS_2H$	$CH_2{=}CH{-}C_6H_5$	28	129-131	0.1	1.5381	1.0990	9.73	9.82/9.92
$(iso\text{-}C_3H_7O)_2PS_2H$	$CH_2{=}CH{-}C_6H_5$	38.5	121-124	0.2	1.5365	1.0966	9.73	9.81/9.95
$(C_4H_9O)_2PS_2H$	$CH_2{=}CH{-}C_6H_5$	13	137-140	0.025	1.5320	1.0890	8.94	8.82/8.8
$(iso\text{-}C_4H_9O)_2PS_2H$	$CH_2{=}CH{-}C_6H_5$	17.5	117-122	0.04	1.5301	1.0860	8.94	9.1/9.18

TABLE 2

Mixed Esters of Dithiophosphoric Acid Obtained by Interaction of Dithiophosphoric Acid with Unsaturated Alcohols and Esters

Initial compound		Yield	Boiling point (°)	Pressure (in mm)	n_D^{20}	d_4^{20}	Phosphorus analysis	
							P calc'd (%)	P found (%)
$(CH_3O)_2PS_2H$	$CH_2{=}CHOCOCH_3$	38	100-103	2	1.5252	1.1558	12.63	13.3 13.4
$(C_2H_5O)_2PS_2H$	$CH_2{=}CHOCOCH_3$	71	115-117	1.5	1.4948	1.1517	11.4	11.37 11.34
$(C_3H_7O)_2PS_2H$	$CH_2{=}CHOCOCH_3$	46	80- 81	0.05	1.5075	1.0984	10.32	9.90 9.92
$(iso\text{-}C_3H_7O)_2PS_2H$	$CH_2{=}CHOCOCH_3$	50	72-74	0.1	1.4335	1.0846	10.32	10.9 10.8
$(iso\text{-}C_4H_9O)_2PS_2H$	$CH_2{=}CHOCOCH_3$	43	104	0.075	1.4858	1.0926	9.43	9.96 10.1
$(C_4H_9O)_2PS_2H$	$CH_2{=}CHOCOCH_3$	25	109	0.4	1.4915	1.0915	9.43	10.22 10.48
$(C_4H_9O)_2PS_2H$	$CH_2{=}CHCH_2OH$	14.1	90- 95	0.03	1.4835	1.0491	10.31	10.21 10.02

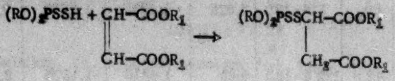
TABLE 3

Mixed Esters of Dithiophosphoric Acid Obtained from Dithiophosphoric Acids and the Esters of Unsaturated Acids

Initial compound		Yield	Boiling point (°)	Pressure (in mm)	n_D^{20}	d_4^{20}	Phosphorus analysis	
							P calc'd (%)	P found (%)
$(CH_3O)_2PS_2H$	$CH_2{=}CHCOOCH_3$	67	145	3	1.5160	1.2625	12.69	12.71 12.78
$(C_2H_5O)_2PS_2H$	$CH_2{=}CHCOOCH_3$	83	167	1.5	1.5050	1.1911	11.38	11.92 11.98
$(iso\text{-}C_4H_9O)_2PS_2H$	$CH_2{=}CHCOOCH_3$	58	124-129	0.2	1.4915	1.1172	9.43	9.62 9.72
$(CH_3O)_2PS_2H$	$CH_2{=}C(CH_3)COOCH_3$	38	133-135	2	1.5100	1.2330	12.01	12.01 12.0
$(C_2H_5O)_2PS_2H$	$CH_2{=}C(CH_3)COOCH_3$	59	154.5	5	1.4995	1.1577	10.82	11.31 11.35
$(iso\text{-}C_3H_7O)_2PS_2H$	$CH_2{=}C(CH_3)COOCH_3$	47	84-85	0.02	1.4935	1.1203	9.84	10.15 10.28
$(iso\text{-}C_4H_9O)_2PS_2H$	$CH_2{=}C(CH_3)COOCH_3$	56	115-116	0.04	1.4915	1.1138	9.05	9.32 9.16
$(C_4H_9O)_2PS_2H$	$CH_2{=}C(CH_3)COOCH_3$	38	110	0.025	1.4918	1.1132	9.05	8.8 9.14

Addition of dithiophosphoric acids to acrylonitrile and maleic acid esters proceeds quite easily. This reaction can be represented by schemes 6 and 7 :

$$(RO)_2PSSH + CH_2{=}CHCN \rightarrow (RO)_2PSSCH_2CH_2CN. \qquad (6)$$



$$(RO)_2PSSH + \begin{matrix} CH{-}COOR_1 \\ \| \\ CH{-}COOR_1 \end{matrix} \rightarrow \begin{matrix} (RO)_2PSSCH{-}COOR_1 \\ | \\ CH_2{-}COOR_1 \end{matrix} \qquad (7)$$

The compounds obtained by the authors, with their properties, are given in Tables 4 and 5.

TABLE 4

Mixed Esters of Dithiophosphoric Acid Synthesized from Dialkyldithiophosphoric Acids and Acrylonitrile

Initial compound		Yield	Boiling point (°)	Pressure (in mm)	n_D^{20}	d_4^{20}	Phosphorus analysis P calc'd (%)	 P found (%)
$(C_2H_5O)_2PS_2H$	$CH_2{=}CHCN$	33	137-142	3.5	1.5195	1.1704	12.93	12.75 12.88
$(C_3H_7O)_2PS_2H$	$CH_2{=}CHCN$	30	116-120	0.05	1.5068	1.0505	11.59	11.98 11.71
$(C_4H_9O)_2PS_2H$	$CH_2{=}CHCN$	27.5	121-123	0.03	1.5050	1.0816	10.5	10.51 10.61
iso-$(C_4H_9O)_2PS_2H$	$CH_2{=}CHCN$	44	122-123	0.05	1.5010	1.0986	10.5	10.81 11.0
iso-$(C_3H_7O)_2PS_2H$	$CH_2{=}CHCN$	44.7	98-99	0.05	1.5020	1.0182	11.59	12.05 11.91

TABLE 5

Mixed Esters of Dithiophosphoric Acid Synthesized from Dialkyldithiophosphoric Acids and Esters of Maleic Acid.

Initial compound Dialkyldithiophosphoric acid	 Olefin	Yield	Boiling point (in °)	Pressure (in mm)	n_D^{20}	d_4^{20}	Phosphorus analysis P calc'd (%)	 P found (%)
1	2	3	4	5	6	7	8	9
$(CH_3O)_2PS_2H$	$CH{-}COOC_2H_5$ $\|$ $CH{-}COOC_2H_5$	50	160-170	3.5	1.4960	1.2076	9.36	8.95 8.70
$(C_2H_5O)_2PS_2H$	$CH{-}COOC_2H_5$ $\|$ $CH{-}COOC_2H_5$	59	157-162	3	1.4910	1.1742	8.65	8.62 8.50
$(C_3H_7O)_2PS_2H$	$CH{-}COOC_2H_5$ $\|$ $CH{-}COOC_2H_5$	27	145	0.1	1.4680	1.1706	8.03	8.30 8.42
iso-$(C_3H_7O)_2PS_2H$	$CH{-}COOC_2H_5$ $\|$ $CH{-}COOC_2H_5$	39	161	4	1.5440	1.0702	8.03	8.32 8.30
$(C_4H_9O)_2PS_2H$	$CH{-}COOC_2H_5$ $\|$ $CH{-}COOC_2H_5$	40	125-128	0.025	1.4861	1.1078	7.5	7.72 7.92
iso-$(C_4H_9O)_2PS_2H$	$CH{-}COOC_2H_5$ $\|$ $CH{-}COOC_2H_5$	15	117-130	0.04	1.4855	1.0642	7.5	7.94 7.84
$(CH_3O)_2PS_2H$	$CH{-}COOCH_3$ $\|$ $CH{-}COOCH_3$	34.1	134.5	0.2	1.5070	1.2864	10.24	10.55 10.62

TABLE 5 — (continued)

1	2	3	4	5	6	7	8	9
$(C_2H_5O)_2PS_2H$	$CH{-}COOCH_3$ ‖ $CH{-}COOCH_3$	50	116-120	0.025	1.4985	1.2237	9.38	9.47 9.50
$(CH_3O)_2PS_2H$	$CH{-}COOC_3H_7$-iso ‖ $CH{-}COOC_3H_7$-iso	42.8	122.5-123	0.05	1.4810	1.1824	8.64	8.31 8.38
$(C_2H_5O)_2PS_2H$	$CH{-}COOC_3H_7$-iso ‖ $CH{-}COOC_3H_7$-iso	67.2	117-121	0.025	1.4815	1.1493	8.01	8.54 8.57
$(C_3H_7O)_2PS_2H$	$CH{-}COOC_3H_7$-iso ‖ $CH{-}COOC_4H_7$-iso	43.5	125-128	0.075	1.4785	1.1146	7.47	7.61
$(CH_3O)_2PS_2H$	$CH{-}COOC_3H_9$-iso ‖ $CH{-}COOC_4H_9$-iso	43.1	127.5-128	0.03	1.4835	1.1483	8.01	7.50 7.48
$(C_2H_5O)_2PS_2H$	$CH{-}COOC_4H_9$-iso ‖ $CH{-}COOC_4H_9$-iso	42.6	124-128	0.02	1.4775	1.1098	7.47	7.32 7.14
$(C_3H_7O)_2PS_2H$	$CH{-}COOC_4H_5$-iso ‖ $CH{-}COOC_4H_9$-iso	35.1	143-145	0.05 - 0.06	1.4822	1.0957	6.99	6.74 6.69

TABLE 6

Mixed Esters of Dithiophosphoric Acid Containing the Carboxyl Group

Initial compound		Yield	Boiling point (°)	Pressure (in mm)	n_D^{20}	d_4^{20}	Phosphorus analysis	
							P calc'd (%)	P found (%)
$(C_3H_7O)_2PS_2H$	$CH_2{=}CHCHO$	37	74	0.15	1.5040	1.1348	11.5	11.90 11.28
$(C_2H_5O)_2PS_2H$	$CH_2{=}CHCHO$	34	80-81	0.05	1.5070	1.0984	12.85	12.90 13.00
$(C_4H_9O)_2PS_2H$	$CH_2{=}CHCHO$	28	75-77	0.025	1.4955	1.0756	10.37	9.87 9.88
$(CH_3O)_2PS_2H$	$(CH_3)_2C{=}CHCOCH_3$	70	93-96	0.05	1.5265	1.1979	12.08	12.41 12.27

Dialkyldithiophosphoric acids add with comparative ease to aldehydes and ketones as well.

$$(RO)_2PSSH + CH_2{=}CHCHO \rightarrow (RO)_2PSSCH_2CH_2CHO.$$

Compounds synthesized are given in Table 6.

EXPERIMENTAL

The synthesis of mixed dithiophosphoric acid esters was carried out in practically all cases under the following standard conditions: 1 mole of dialkyldithiophosphoric acid was gradually added, with good stirring, to 1 mole of olefin. The addition was carried out at such a rate that the temperature of the reaction mixture did not exceed 40-50°. After having added all of the dialkyldithiophosphoric acid, the reaction mixture was kept at room temperature until there was no further change in the free dialkyldithiophosphoric acid content, as determined by special titration tests with 0.1 N sodium hydroxide Unreacted olefin was then distilled out of the reaction mixture and the residue fractionated in vacuo.

The initial dialkyldithiophosphoric acid was synthesized by interaction of phosphorous pentasulfide with the corresponding alcohol [17].

SUMMARY

The reaction of dialkyldithiophosphoric acids with various unsaturated compounds has been studied. It has been demonstrated that satisfactory yields of mixed dithiophosphoric acid esters result on interaction of the compounds with dialkyldithiophosphoric acids.

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* VASKhNIL. = Lenin All-Union Academy of Agricultural Sciences.

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SUMMARY

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ORGANIC INSECTOFUNGICIDES

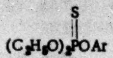
XV. SYNTHESIS OF ESTERS OF THIOPHOSPHORIC ACID CONTAINING VARIOUS SUBSTITUENTS IN THE AROMATIC RADICAL

N. N. Melnikov and D. N. Khokhlov

It has been recently demonstrated that certain esters of thiophosphoric acid possess quite a high insecticidal activity [1], and diethyl-4-nitrophenylthiophosphate has already found extensive application in agriculture [2-6]. However, under field conditions, diethyl-4-nitrophenylthiophosphate loses activity rather rapidly, which is related both to partial evaporation of the preparation and to its photochemical decomposition under field conditions. It should be noted that for combating certain plant pests, preparations with a longer duration of action are required.

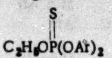
With respect to the above-stated, the authors instigated a special investigation on the synthesis of various thiophosphoric acid esters containing halogens and nitro groups in the aromatic ring. Synthesis of these esters is also of interest for a study of relation between the compound and the insecticidal activity of the thiophosphoric acid esters.

The authors have synthesized esters of the general formula:



$(C_2H_5O)_2\overset{S}{\overset{\|}{P}}OAr$

(I)



$C_2H_5O\overset{S}{\overset{\|}{P}}(OAr)_2$

(II)

$(ArO)_3PS$

(III)

The compounds obtained, and their properties, are presented in Tables 1, 2 and 3. Some of these compounds are described in the entomological literature, but their constants are not given [7].

Aside from the ethyldiarylthiophosphates listed in Table 1, the authors have also synthesized corresponding esters, using ethyldichlorothiophosphate with isomeric chloronitrophenols and with tetrachlorophenol. The resulting substances were oily liquids, distilling in vacuo with decomposition. It was not possible to separate them in the pure form.

Diethylarylthiophosphates were obtained by the interaction of diethylchlorothiophosphate with the corresponding phenolate in chlorobenzene or toluene, in the presence of pyridine as catalyst [8].

$$(C_2H_5O)_2PSCl + ArONa \rightarrow (C_2H_5O)_2PSOAr \tag{1}$$

Ethyldiarylthiophosphates were synthesized under similar conditions from ethyldichlorothiophosphate and the phenolates.

$$C_2H_5OPSCl_2 + 2ArONa \rightarrow C_2H_5OPS(OAr)_2 \tag{2}$$

The triarylthiophosphates were obtained from phosphorous thiotrichloride and the phenolates:

$$PSCl_3 + 3ArONa \rightarrow (ArO)_3PS. \tag{3}$$

It was of interest to note that tris-(chloronitrophenyl)-thiophosphates were obtained not only by interaction of phosphorous thiotrichloride with the corresponding phenolates, but also by reaction of the phenolates with ethyldichlorothiophosphate and diethylchlorothiophosphate. In this case the reaction apparently proceeds in quite a complex manner. There is formed at first from the diethylchlorothiophosphate and phenolate the diethylarylthiophosphate according to Reaction (1), which then becomes symmetrical to give a mixture of esters:

$$3(C_2H_5O)_2PSOAr \rightarrow 2(C_2H_5O)_3PS + (ArO)_3PS \tag{4}$$

Ethyldichlorothiophosphate apparently reacts in like manner:

$$3C_2H_5OPS(OAr)_2 \rightarrow (C_2H_5O)_3PS + 2(ArO)_3PS \tag{5}$$

TABLE 1
Properties of Diethylarylthiophosphates

Name and formula	Yield (in %)	B.p. or M.p.	d_4^{20}	n_D^{20}	Found %		Calculated %	
					Halogen	Sulfur	Halogen	Sulfur
$(C_2H_5O)_2PSOC_6H_4Cl$-(2) Diethyl-2-chlorophenylthiophosphate	78	93-99° 0.2 mm	1.2223	1.5208	12.16 11.96	11.05 11.40	12.63	11.42
$(C_2H_5O)_2PSOC_6H_4Cl$-(3) Diethyl-3-Chlorophenylthiophosphate	88	95 0.1 mm	1.2242	1.5218	12.83 12.78	11.10 11.35	12.63	11.42
$(C_2H_5O)_2PSOC_6H_4Cl$-(4) Diethyl-4-chlorophenylthiophosphate	83	96-102 0.15 mm	1.2277	1.5221	–	–	–	–
$(C_2H_5O)_2PSOC_6H_3Cl_2$-(2, 4) Diethyl-2, 4-dichlorophenylthiophosphate	66	106-108 0.15 mm	1.3045	1.5340	–	–	–	–
$(C_2H_5O)_2PSOC_6H_3Cl_2$-(2, 6) Diethyl-2, 6-dichlorophenylthiophosphate	83	106-109 0.1 mm	1.2963	1.5338	22.83 22.76	10.19 10.06	22.50	10.17
$(C_2H_5O)_2PSOC_6H_2Cl_3$-(2, 4, 5) Diethyl-2, 4, 5-trichlorophenylthiophosphate	69	125-128 0.025 mm	1.3695	1.5412	30.34 30.08	8.90 8.85	30.43	9.14
$(C_2H_5O)_2PSOC_6H_2Cl_3$-(2, 4, 6) Diethyl-2, 4, 6-trichlorophenylthiophosphate	72	M.p. 55- 56°	–	–	30.48 30.42	9.16 8.97	30.43	9.14
$(C_2H_5O)_2PSOC_6HCl_4$-(2, 3, 4, 6) Diethyl-2, 3, 4, 6-tetrachlorophenylthiophosphate	93	M.p. 45- 46°	–	–	37.35 37.29	8.13 8.20	36.81	8.31
$(C_2H_5O)_2PSOC_6Cl_5$ Diethylpentachlorophenylthiophosphate	80	M.p. 95- 96°	–	–	42.44 42.87	7.53 7.51	42.46	7.66
$(C_2H_5O)_2PSOC_6H_4Br$-(2) Diethyl-2-bromophenylthiophosphate	76	100-104 0.01 mm	1.4036	1.5401	24.78 24.25	9.50 9.82	24.58	9.86
$(C_2H_5O)_2PSOC_6H_4Br$-(4) Diethyl-4-bromophenylthiophosphate	62	111-115 0.01 mm	1.3902	1.5356	24.70 24.66	9.70 10.12	24.58	9.86
$(C_2H_5O)_2PSOC_6H_4I$-(2) Diethyl-2-iodophenylthiophosphate	79	125-130 0.05 mm	1.5733	1.5691	33.97 34.18	8.53 8.73	34.10	8.62
$(C_2H_5O)_2PSOC_6H_4I$-(4) Diethyl-4-iodophenylthiophosphate	70	116-118 0.03 mm	1.5817	1.5680	34.46 34.30	8.25 8.53	34.10	8.62
$(C_2H_5O)_2PSOC_6H_3NO_2$-(4)Cl-(2) Diethyl-2-chloro-4-nitrophenylthiophosphate	47	115-120 0.06 mm	1.3612	1.5482	10.95 11.01	9.38 9.56	10.89	9.85
$(C_2H_5O)_2PSOC_6H_3NO_2$-(2)Cl-(4) Diethyl-4-chloro-2-nitrophenylthiophosphate	44	105-111 0.03 mm	1.3115	1.5308	10.78 11.07	9.49 9.45	10.89	9.85
$(C_2H_5O)_2PSOC_6H_2NO_2$-(4)Cl_2-(2, 6) Diethyl-2, 6-dichloro-4-nitrophenylthiophosphate	66	135-140 0.075 mm	1.4112	1.5528	19.92 19.82	9.24 8.55	19.69	8.90

Tests of the compounds synthesized on the granary weevil indicated that none of them surpass diethyl-4-nitrophenylthiophosphate in insecticidal activity.

EXPERIMENTAL

1. Synthesis of Diethylarylthiophosphates. Synthesis of diethylarylthiophosphates was carried out according to a somewhat modified method of Toy [8]. A drop of pyridine was added to potassium or sodium phenolate suspended in chlorobenzene or toluene, and an equimolecular quantity of diethylchlorothiophosphate then added. After addition of all of the diethylchlorothiophosphate, the reaction was heated, with good stirring and with a reflux condenser, at 100-130° to the disappearance of all phenolate (from 10 minutes to 20 hours). Following termination of the reaction, the potassium or sodium chloride was filtered off, the filtrate washed with sodium hydroxide solution to

TABLE 2
Properties of Ethyldiarylthiophosphates

Name and formula	Yield in %	B.p. or M.p.	d_4^{20}	n_D^{20}	Found %		Calculated %	
					Halogen	Sulfur	Halogen	Sulfur
$C_2H_5OPS[OC_6H_4Cl-(2)]_2$ Ethyl-bis-(2-chlorophenyl)-thiophosphate	80	128-132° 0.025 mm	1.2987	1.5693	19.00 19.30	8.45 8.25	19.53	8.83
$C_2H_5OPS[OC_6H_4Cl-(3)]_2$ Ethyl-bis-(3-chlorophenyl)-thiophosphate	87	135-140° 0.05 mm	1.2966	1.5645	19.84 19.94	9.05 8.91	19.53	8.83
$C_2H_5OPS[OC_6H_4Cl-(4)]_2$ Ethyl-bis-(4-chlorophenyl)-thiophosphate	80	140-146° 0.05 mm	1.3353	1.5713	19.73 20.07	8.44 8.49	19.53	8.83
$C_2H_5OPS[OC_6H_3Cl_2-(2,4)]_2$ Ethyl-bis-(2,4-dichlorophenyl)-thiophosphate	74	141-146° 0.025 mm	1.4627	1.5962	33.23 33.11	7.10 7.28	32.82	7.42
$C_2H_5OPS[OC_6H_3Cl_2-(2,6)]_2$ Ethyl-bis-(2,6-dichlorophenyl)-thiophosphate	77	M.p. 53-54	–	–	32.80 32.92	7.25 7.35	32.82	7.42
$C_2H_5OPS[OC_6H_2Cl_3-(2,4,5)]_2$ Ethyl-bis-(2,4,5-trichlorophenyl)-thiophosphate.	77	M.p. 68	–	–	42.66 42.50	5.99 6.04	42.46	6.40
$C_2H_5OPS[OC_6H_2Cl_3-(2,4,6)]_2$ Ethyl-bis-(2,4,6-trichlorophenyl)-thiophosphate	65	M p. 112-113	–	–	42.29 42.59	6.55 6.87	42.46	6.40
$C_2H_5OPS(OC_6Cl_5)_2$ Ethyl-bis-(pentachlorophenyl)-thiophosphate	57	M.p. 156-157	–	–	55.10 55.16	5.38 5.53	55.51	5.02
$C_2H_5OPS[OC_6H_4Br-(2)]_2$ Ethyl-bis-(2-bromophenyl)-thiophosphate	70	165 0.25 mm	1.6246	1.5958	35.12 35.71	6.72 6.97	35.35	7.09
$C_2H_5OPS[OC_6H_4Br-(4)]_2$ Ethyl-bis-(4-bromophenyl)-thiophosphate	79	157-160 0.025 mm	1.6165	1.5940	35.62 35.65	6.74 6.62	35.35	7.09
$C_2H_5OPS[OC_6H_4I-(2)]_2$ Ethyl-bis-(2-iodophenyl)-thiophosphate	79	M.p. 47-48	–	–	46.51 46.89	5.87 6.03	46.48	5.87
$C_2H_5OPS[OC_6H_4I-(4)]_2$ Ethyl-bis-(4-iodophenyl)-thiophosphate	90	M.p. 55-56	–	–	46.69 47.04	6.01 6.08	46.48	5.87

TABLE 3 Properties of Triarylthiophosphates

Name and formula	Yield in %	B.p. or M.p.	d_4^{20}	n_D^{20}	Found %		Calculated %	
					Halogen	Sulfur	Halogen	Sulfur
$PS[OC_6H_4Cl-(2)]_3$ Tris-(2-chlorophenyl)-thiophosphate	84	160-170° 0.025 mm	1.3899	1.5992	23.04 23.49	7.42 7.08	23.87	7.19
$PS[OC_6H_4Cl-(3)]_3$ Tris-(3-chlorophenyl)thiophosphate	94	170-180° 0.05 mm	1.4318	1.6002	23.92 24.11	6.94 7.09	23.87	7.19
$PS[OC_6H_4Cl-(4)]_3$ Tris-(4-chlorophenyl)-thiophosphate	72	M.p. 85-86	–	–	24.14 24.07	7.41 7.00	23.87	7.19
$PS[OC_6H_3Cl_2-(2,4)]_3$ Tris-(2,4-dichlorophenyl)-thiophosphate	70	M.p. 98-99	–	–	38.57 38.96	6.05 6.02	38.73	5.84
$PS[OC_6H_3Cl_2-(2,6)]_3$ Tris-(2,6-dichlorophenyl)-thiophosphate	79	M.p. 101-102	–	–	38.76 38.36	5.47 5.43	38.73	5.84

TABLE 3 – (continued)

Name and formula	Yield in %	B.p. or M.p.	d_4^{20}	n_D^{20}	Found %		Calculated %	
					Halogen	Sulfur	Halogen	Sulfur
$PS[OC_6H_2Cl_3\text{-}(2,4,5)]_3$ Tris-(2,4,5-trichlorophenyl)-thiophosphate	88	M.p. 154-155	–	–	49.11 48.66	4.61 4.76	48.92	4.91
$PS[OC_6H_2Cl_3\text{-}(2,4,6)]_3$ Tris-(2,4,6-trichlorophenyl)-thiophosphate	71	M.p 125-126	–	–	49.28 49.44	4.47 4.83	48.92	4.91
$PS[OC_6HCl_4\text{-}(2,3,4,6)]_3$ Tris-(2,3,4,6-tetrachlorophenyl)-thiophosphate	94	M.p. 136-137*	–	–	56.20 56.29	4.43 4.35	56.31	4.24
$PS[OC_6H_4Br\text{-}(2)]_3$ Tris-(2-bromophenyl)-thiophosphate	59	M.p 89-90	–	–	41.57 41.43	5.59 5.33	41.40	5.54
$PS[OC_6H_4Br\text{-}(4)]_3$ Tris-(4-bromophenyl)-thiophosphate	82	M.p. 89-90	–	–	41.42 41.65	5.37 5.10	41.40	5.54
$PS[OC_6H_4I\text{-}(2)]_3$ Tris-(2-iodophenyl)-thiophosphate	71	M.p. 147-148	–	–	53.18 53.24	4.65 4.62	52.88	4.46
$PS[OC_6H_4I\text{-}(4)]_3$ Tris-(4-iodophenyl)-thiophosphate	68	M.p. 123-124	–	–	53.04 53.21	4.68 4.83	52.88	4.46
$PS[OC_6H_3NO_2\text{-}(4)Cl\text{-}(2)]_3$ Tris-(2-chloro-4-nitrophenyl)-thiophosphate	72	M.p. 186-187	–	–	18.33 18.55	5.51 5.25	18.31	5.52
$PS[OC_6H_3NO_2\text{-}(2)Cl\text{-}(4)]_3$ Tris-(4-chloro-2-nitrophenyl)-thiophosphate	70	M.p. 136-137	–	–	18.04 18.41	5.45 5.57	18.31	5.52
$PS[OC_6H_2NO_2\text{-}(4)Cl_2\text{-}(2,6)]_3$ Tris-(2,6-dichloro-4-nitrophenyl)-thiophosphate	57	M.p. 212-213	–	–	31.48 31.31	4.84 5.16	31.12	4.69

remove completely all free phenol, then washed with water and dried over calcium chloride. The solvent was distilled off in vacuo (at 3-5 mm) at 120-140°. The residue was distilled in high vacuum, or recrystallized from a suitable solvent to constant melting point.

2. Ethyldiarylthiophosphate and Triarylthiophosphate Synthesis. Synthesis of ethyldiarylthiophosphate was carried out under the same conditions as for the synthesis of diethylarylthiophosphates. 2 moles of phenolate was used for 1 mole of ethyldichlorothiophosphate. The triarylthiophosphates were also obtained under the same conditions from phosphorous thiotrichloride and the phenolates.

3. Interaction of 2-Chloro-4-nitrophenolate of Sodium with Diethylchlorothiophosphate. Under the conditions described, and from 5 g of sodium phenolate and 4.6 g of diethylchlorothiophosphate in 25 ml of chlorobenzene, there was obtained after suitable treatment 4.5 g of oil, part of which crystallized. The crystals were filtered off, washed with ethyl ether (yield 1.2 g), and recrystallized twice from benzene (yield 0.4 g). The melting point was 186-187°

Found %: Cl 18.98, 18.62; S 5.57, 5.61. $C_{18}H_9Cl_3O_9N_3SP$. Calculated %: Cl 18.31; S 5.52.

4. Interaction of 4-Chloro-2-nitrophenolate of Sodium with Diethylchlorothiophosphate. 5.5 g of the oil was obtained by the conditions described above, from 5 g of 4-chloro-2 nitrophenolate of sodium, 4.6 g of diethylchlorothiophosphate in 25 ml of chlorobenzene, after many hours of heating, followed by removal of the sodium chloride and distillation of the chlorobenzene.

After recrystallization of the crystallized portion of the material from ligroin, 1.1 g of the tris-(4-chloro-2-nitrophenyl)-thiophosphate, with m.p. 136 - 137° was obtained.

Found %: Cl 18.38, 18.61; S 5.15, 4.98. $C_{18}H_9Cl_3O_9N_3SP$. Calculated %: Cl 18.31; S 5.52

5. Interaction of the 2-Chloro-4-nitrophenolate of Potassium with Ethyldichlorothiophosphate. From 4.5 g of potassium phenolate and 2 g of ethyldichlorothiophosphate, under the above-described conditions, with 3 hours heating at 125 - 130° and appropriate treatments, 2.5 g of oil plus precipitate resulted The oil was diluted with ether and the precipitate filtered off. After a double recrystallization from acetone, 0.4 g of the pure tris-(2-chloro-4-nitrophenyl)-thiophosphate was obtained with m.p. 186 - 187°.

Found %: Cl 18.33, 18.55; S 5.51, 5.25. $C_{18}H_9Cl_3O_9N_3SP$. Calculated %: Cl 18.31; S 5.52.

6. Interaction of Sodium 4-Chloro-2-nitrophenolate with Ethyldichlorothiophosphate. 1.1 g of pure tris-(4-chloro-2-nitrophenyl)-thiophosphate with m.p. 136 - 137° was obtained under the experimental conditions of "5" above, using 5 g of sodium phenolate, and 2.2 g of ethyldichlorothiophosphate.

Found %: Cl 18.04, 18.41; S 5.41, 5.57. $C_{18}H_9Cl_3O_9NSP$. Calculated %: Cl 18.31; S 5.52

SUMMARY

1. A series of esters of thiophosphoric acid, which have not been described in the literature, have been synthesized for the purpose of studying their insecticidal properties

2. It has been established that apart from the normal reaction course, ethyldichlorothiophosphate and diethylchlorothiophosphate with chloronitrophenolate may produce triarylthiophosphates, the formation of which can be represented by Reactions (4) and (5).

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EFFECTS OF THE NATURE AND POSITION OF SUBSTITUENTS IN PHENYL RADICALS (Ar').ArNHCOC(OH)Ar'$_2$ UPON 5-MEMBERED HETEROCYCLE CLOSURE. XIX.

P. A. Petyunin and V. S. Shklyaev

One of us with I. S. Berdinsky [1] has demonstrated, in the case of ring closure for benzyl and p-tolyl acid arylamides, that the structure of the radicals on the carbinol carbon atoms exerts a profound effect upon the reaction rate. Following the period of elucidation of the mechanism of intramolecular condensations of hydroxycarboxylic acid arylamides [2], it was then possible to clarify these facts and to design further investigational procedures. As is known, strain in ring formation and distance between reactive terminal groups [3,4] has an effect upon formation of cyclic systems. In forming rings of the same type, in our case of 5-membered rings, the indicated factors are of the same degree, and distinctions in ease of ring closure are thus caused by other factors.

For the present work compounds of the type ArNHCOC(OH)Ar$'_2$, where Ar = m-ClC$_6$H$_4$–, p-ClC$_6$H$_4$–, p-BrC$_6$H$_4$– o-CH$_3$C$_6$H$_4$– p-CH$_3$C$_6$H$_4$–, o-CH$_3$OC$_6$H$_4$–, m-CH$_3$OC$_6$H$_4$–, and p-CH$_3$OC$_6$H$_4$– were used as the starting materials.

The rate at which 5-membered heterocyclic closure took place in the indicated compounds was determined according to the following method: the optimun quantity of concentrated sulfuric acid was added along the wall of the test tube to 1 ml of the solution (0.015 mole of arylamide per liter of glacial acetic acid) at the given temperature. The reaction mass was kept at the same temperature for 1 minute on a water bath. Upon stirring, the coloration which appeared, depending upon the arylamide structure, disappeared after various time intervals. The appearance and disappearance times of color were determined by a second-meter, and were the rate indicator for ring closure (Table 1).

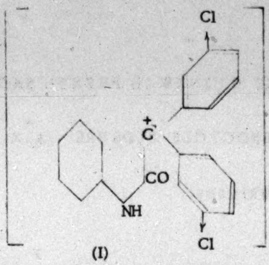
TABLE 1

Closure Rate for 5-Membered Heterocycles with Arylamides of *a*-Hydroxycarboxylic Acids

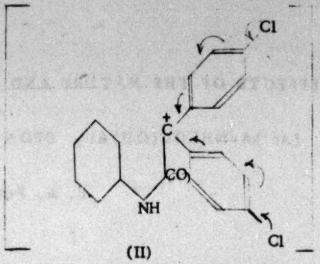
No.	Formulas	Quantity of concentrated H_2SO_4 (in ml)	Ring closure rate at 20°
1	$C_6H_5NHCOC(OH)(C_6H_4Cl\text{-}m)_2$	7.5	Very high
2	$C_6H_5NHCOC(OH)(C_6H_4Cl\text{-}p)_2$	4	12.5
3	$C_6H_5NHCOC(OH)(C_6H_4Br\text{-}p)_2$	4	5
4	$C_6H_5NHCOC(OH)(C_6H_4CH_3\text{-}p)_2$	1.5	12
5	$o\text{-}CH_3OC_6H_4NHCOC(OH)(C_6H_4OCH_3\text{-}p)_2$	0.1	1
6	$C_6H_5NHCOC(OH)(C_6H_4CH_3\text{-}o)_2$	2.5	1800

Note: Here and elsewhere the closure rate of the heterocycle is expressed in relative numbers. The rate of cyclic closure for arylamide No. 5 equal to 300 minutes, was taken as unity. Optimal quantities of sulfuric acid were used; they were determined for each arylamide, and represented the minimal amount for ensuring completeness of conversion of the arylamide into the heterocyclic compound. An increase in the quantity of sulfuric acid decreases markedly the rate of ring closure; a two-fold increase in the amount cuts down the condensation rate almost six-fold [2,5]. In the experiment involving the β-napthalide of 4,4'-dimethoxybenzylic acid, a 75-fold increase in quantity of sulfuric acid decreased the ring closure rate almost 750-fold.

It can be seen from Table 1 that the closure rate for 5-membered heterocycles fluctuates from 1 to 1800; and more. The highest rate of closure takes place with arylamide No. 1. As a result of the electron-accepting action of the chlorine atom, coupling of π-electrons of the benzene rings with carbonium carbon (1) decreases, and the degree of electrophilic attack of the latter increases, that is, is reflected in an extremely high reaction rate.



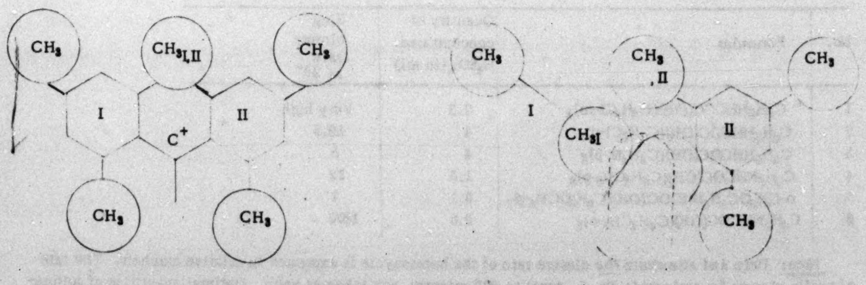
(I)



(II)

With arylamides Nos. 2 and 3 containing halogen in the p-position, the heterocycle closes at a slow rate. Under influence of the carbon atom positive charge the electron-donating properties of the halogens are intensified and the decrease in rate of cyclic closure can be explained by the presence of cation coupling with participation of the halogen atoms (II). The cyclization rate decreases upon introducing electron-donating substituents (arylamide No. 4) into the p-position; an even greater decrease takes place with arylamide No. 5. This is explained by the presence of cation coupling with participation of oxygen atoms of the methoxy group. With arylamide No. 6, the heterocycle closes 150-fold more rapidly than its p-isomer (arylamide No. 4). When substituents are introduced into the o-position, planarity of the cation is disrupted and coupling of the carbonium carbon with aryl radicals decreases [6], which therefore leads to considerable acceleration of ring formation.

It can be seen from the data given that ring closure rate is determined both by the nature of the substituent groups and by their position. It is of interest to compare the ease of ring closure for all possible isomers of arylamides with the same substituents on the phenyl radicals at the carbonyl carbon. With this object in mind, the rate of the heterocyclic closure for α-napththylides of 2,2'-, 3,3'- and 4,4'-dimethoxybenzylic acids was determined. It was found that the cyclic closure rate for the meta isomer at 20° with 0.5 ml of H_2SO_4 was equal to 1200, and for the ortho-isomer with 1.5 ml, equal to 37.5, and for the para isomer with 0.1 ml, equal to 5.



Thus, from the point of view of substituent positions, the cyclic closure rate decreases in the order m > o > p.

With respect to the theoretical relationship, it was important to study the possibility of intramolecular ring closure for those arylamides in which all four ortho-positions of the phenyl radicals at the carbinol carbon are occupied by substituents. For this purpose the o-anisidide of dimesityiglycolic acid was synthesized. An attempt to close the ring failed. Steric hindrance is strongly exhibited for the cation of the halochromic salt of this arylamide, barring the possibility of a planar arrangement of the mesityl radicals (Fig. 1). Because of this, radicals are arranged in interperpendicular planes. Here the $CH_{3_{I}}$ group (Fig. 2) coming in contact with the benzene ring bound with nitrogen (drawn as a broken line) mitigates against a position favorable for closure of a 5-membered planar ring.

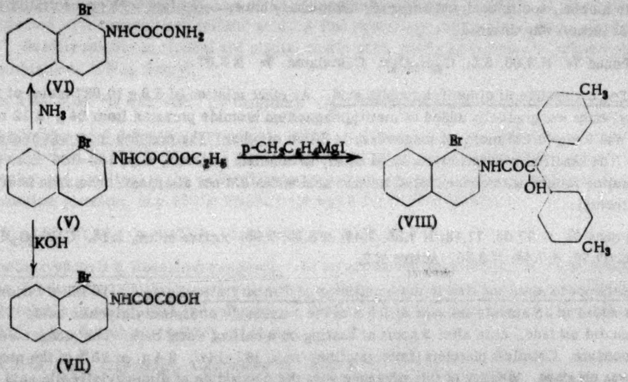
It has been further established that with α and β-naphthalides of 4,4'-dimethoxybenzylic acid, cyclic closure proceeds at varied speed (Table 2).

TABLE 2

Closure Rates of 5-Membered Heterocycles for α- and β-Naphthalides of 4,4'-Dimethoxybenzylic Acid.

Formula	Quantity of conc. H_2SO_4 (in ml)	Ring closure rate at 20°
β-$C_{10}H_7NHCOC(OH)(C_6H_4OCH_3\text{-}p)_2$ (III)	0.1	1.25
α-$C_{10}H_7NHCOC(OH)(C_6H_4OCH_3\text{-}p)_2$ (IV)	0.1	5

Upon condensation (III), the central carbon atom becomes coordinated with the α-position of the naphthyl radical, and with condensation (IV) – the β-position. But if the α-position is more nucleophilic than the β-, the rate of condensation (III) then should be greater than (IV). However, (IV) condenses four times more rapidly than (III), explainable by a lesser steric accessibility of the α-position upon coordination with a central carbon atom containing two phenyl radicals. Similar cases are known [7] in naphthaline reactions. One of us [8] has shown that the 1-bromo-2-naphthalide of benzylic acid forms a β,β-condensation product. In connection with the fact it was of interest to compare cyclic closure rates for α,β- and β,β-condensations. For this purpose, synthesis of the 1-bromo-2-naphthalide of p-tolylic acid was carried out according to the scheme:



The amide (VI) resulted by the action of ammonia upon the ethyl ester of 1-bromo-2-naphthyloxamic acid (V), and upon hydrolysis, 1-bromo-2-naphthyloxamic acid (VII) resulted. The 1-bromo-2-naphthalide of p-tolylic acid (VIII) was synthesized by interacting (V) with p-tolylmagnesium iodide. It was found that the cyclic closure rate for (VIII) at 20°, with 1.5 ml of H_2SO_4, was equal to 12, and for the β-naphthalide of p-tolylic acid (IX) under the same conditions – 11.5. Thus, condensation (VIII) and (IX) rates are almost the same despite the fact that steric hindrances occur with α,β-condensation (IX). The decreased rate of 5-membered ring closure for β,β-condensation (VIII) is explained by a weakening of the nucleophilic reaction center due to manifestation of an electron-accepting action on the part of bromine. The effect of a nucleophilic reaction center upon the condensation of the m-anisidide of p-tolylic acid has been described [1].

EXPERIMENTAL

The anilide of 3,3'-dichlorobenzylic acid. 7.7 g (0.04 mole) of oxanilic acid ethyl ester was added to m-chlorophenylmagnesium iodide obtained from 42.5 g (0.18 mole) of m-chloroiodobenzene and 4.4 g (0.18 mole) of magnesium in 100 ml of ether. The reaction mass was decomposed with 5% hydrochloric acid. The ether layer was separated, and to remove the solvent as well as volatile reaction products, was distilled with steam. An oily liquid was left in the distilling flask, which crystallized rapidly on standing. Long, colorless needles (from toluene), with m.p. 170-171°. Insoluble in water and gasoline; soluble, upon heating, in alcohol, benzene, acetone, toluene, acetic acid, and ether. Formed an evanescent reddish-violet coloration with concentrated sulfuric acid. 7.3 g of the substance was obtained (49% calculating on the basis of the ethyl ester of oxanilic acid taken for reaction).

0.2506 g substance: 14.3 ml 0.05 N H_2SO_4. 0.2957 g substance: 15.9 ml 0.05 N H_2SO_4. Found %: N 3.99, 3.76. $C_{20}H_{15}O_2NCl_2$. Calculated %: N 3.76.

The anilide of 4,4'-dichlorobenzylic acid. Initial substances: 23.6 g (0.1 mole) of p-chloroiodobenzene* 4.3 g (0.0022 mole) of oxanilic acid ethyl ester and 2.3 g (0.1 mole) of magnesium.

After decomposition of the reaction mixture the crystalline mass was isolated from the ether layer. Upon crystallization from benzene—colorless platelets. m.p. 181.5-182.5°. Yield 4.6 g (55% of theory). Soluble, upon heating, in alcohol, benzene, acetic acid, acetone and ether; insoluble in water and gasoline. Reddish-violet coloration with concentrated sulfuric acid, disappearing upon standing or heating.

Found %: N 3.74, 3.94. $C_{20}H_{15}O_2NCl_2$. Calculated %: N 3.76.

The anilide of 4,4'-dibromobenzylic acid. Taken for reaction were: 6.6 g (0.034 mole) of oxanilic acid ethyl ester, 34.4 g (0.15 mole) of p-dibromobenzene and 3.6 g of magnesium. Thin needles (from benzene) with m.p. 192-194°. Insoluble in water and gasoline; soluble in alcohol, ether, benzene and toluene. Violet coloration with concentrated sulfuric acid, fading on standing. Yield was 5.1 g (32.5% of theory).

Found %: N 2.66, 2.76. $C_{20}H_{15}O_2NBr$. Calculated %: N 3.04.

α-Naphthalide of 3,3'-dimethoxybenzylic acid.** Taken for reaction were: 6 g (0.025 mole) of α-naphthyloxamic acid ethyl ester, 29 g (0.13 mole) of m-iodoanisole, 3 g (0.13 mole) of magnesium. The product crystallized as colorless platelets from alcohol, m.p. 151-152.5°. Insoluble in water, gasoline and ether; readily-soluble in alcohol, acetic acid and benzene. Momentary brown coloration with concentrated sulfuric acid. 4.8 g (46.8 % of theory) was obtained.

Found %: N 3.66, 3.5. $C_{26}H_{23}O_4N$. Calculated %: N 3.37.

The o-anisidide of dimesitylglycolic acid. An ether solution of 5.9 g (0.027 mole) of 2-methoxyoxanilic acid ethyl ester was gradually added to mesitylmagnesium bromide prepared from 24 g (0.12 mole) of bromomesitylene and 2.9 g (0.125 mole) of magnesium in 80 ml of ether. The reaction mass was heated on a water bath 4 hours. The reaction products crystallized slowly to colorless platelets, m.p. 162-164° from gasoline. An orange-red coloration formed with concentrated sulfuric acid which did not disappear, even upon heating. Yield was 2.5 g (22% of theory).

Found %: C 77.65, 77.18; H 7.65, 7.47; N 3.05, 2.95. Active H 2.2, 2.15. $C_{27}H_{31}O_3N$. Calculated %: C 77.70; H 7.44; N 3.35. Active H 2.

Attempt to close the ring in the o-anisidine of dimesitylglycolic acid. 10 ml of concentrated sulfuric acid was added to an acetate solution of 0.5 g of the o-anisidide of dimesitylglycolic acid. The orange-yellow coloration did not fade, even after 3 hours of heating on a boiling water bath. The product was isolated by the usual procedure. Colorless platelets (from gasoline), m.p. 162-164°. 0.4 g, or 80% of the product taken for reaction, was obtained. Identity of this substance with the o-anisidide of dimesitylglycolic acid was proved by the mixed melting test.

The amide of 1-bromo-2-naphthyloxamic acid. Ammonia was passed into a solution of 2 g of 1-bromo-2-naphthyloxamic acid ethyl ester in 10 ml of alcohol, with cooling. The resulting white precipitate was filtered off and dried in air. Upon crystallizing from benzene—colorless needles with m.p. 231-232°. 1.75 g was obtained (96.1% of theory). Poorly-soluble in alcohol, ether and gasoline; soluble with heating in benzene and toluene.

Found %: N 9.66, 9.70. $C_{12}H_9O_2N_2Br$. Calculated: N 9.55.

1-Bromo-2-naphthyloxamic acid. 2 g of 1-bromo-2-naphthyloxamic acid ethyl ester was heated with 250 ml of 0.5% sodium hydroxide The hot, transparent solution was acidified with concentrated hydrochloric acid and the resulting precipitate treated by the usual procedures. Fine needles (from benzene), with m.p. 158-159° (with decomposition). 1.8 g was obtained (99% of theory). Readily-soluble in alcohol; soluble in benzene upon heating, difficultly-soluble in gasoline, ether and water.

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* According to the author's data, p-chloroiodobenzene reacts with the iodine atom, which is in agreement with the data of Michalescu and Garagea [9] and which refutes the data of Range [10].

** This substance, as well as its condensation product, 3,3-bis(3-methoxyphenyl)-6,7-benzohydroxyindole, has been synthesized by I. V. Sannikova and N. N. Staroverova.

Found %: N 4.64, 4.61. $C_{12}H_{8}O_{3}NBr$. Calculated %: N 4.77.

1-Bromo-2-naphthalide of 4,4'-dimethylbenzylic acid. Reaction was effected between 6.44 g (0.02 mole) of 1-bromo-2-naphthyloxamic acid ethyl ester and 0.09 mole of p-tolyl magnesium iodide. Crystallized from benzene as colorless needles with m.p. 158-160°. Readily-soluble in ether, toluene and acetic acid, somewhat less so in alcohol, poorly so in gasoline. With concentrated sulfuric acid, slowly gave a fading raspberry-red coloration. The yield was 3.5 g (38% of theory).

Found %: N 2.79, 3.09. $C_{26}H_{22}O_{2}NBr$. Calculated %: N 3.04.

3,3-Bis-(3-chlorophenyl)-hydroxyindole. 3 g of 3,3'-dichlorobenzylic acid anilide was dissolved in 15 ml of concentrated sulfuric acid. After decoloration, the reaction mass was poured into water. Thin needles (from glacial acetic acid) with m.p. 248-250°. Soluble in alcohol, benzene, toluene and acetic acid; insoluble in water and gasoline. Yield was 2 g (70% of theory).

Found %: N 3.68, 3.65. M 332, 333 (camphor). $C_{20}H_{13}ONCl_{2}$. Calculated %: N 3.96. M 354.

3,3-Bis-(4-chlorophenyl)-hydroxyindole. There was taken for reaction 1 g of 4,4'-dichlorobenzylic acid anilide in 10 ml of concentrated sulfuric acid. Upon crystallization from 70% alcohol → needles grouped in clusters, with m.p. 186-187°. Readily-soluble in alcohol, ether, benzene, chloroform and toluene; insoluble in water and gasoline. Yield was 0.5 g (52.3% of theory).

Found %: N 3.74, 3.94; Cl 20.4. M 355.1, 330.8 (in camphor). $C_{20}H_{13}ONCl_{2}$. Calculated %: N 3.96; Cl 20.6. M 354.

3,3-Bis-(4-bromophenyl)-hydroxyindole. 3 g of 4,4'-dibromobenzylic acid anilide in 25 ml of glacial acetic acid was condensed with concentrated sulfuric acid. A fine crystalline powder (from dilute alcohol) with m.p. 198-200°. Readily-soluble in alcohol and glacial acetic acid, poorly so in benzene, toluene and gasoline. 0.9 g was obtained (31% of theory).

Found %: N 3.38, 3.06. M 432, 435.7 (in camphor). $C_{20}H_{13}ONBr_{2}$. Calculated %: N 3.16. M 443.

3,3-Bis-(4-tolyl)-7-bromo-5,6-benzhydroxyindole. Initial substances: 2 g of the 1-bromo-2-naphthalide of 4,4'-dimethylbenzylic acid in 15 ml of glacial acetic acid and 10 ml of concentrated sulfuric acid. Soluble, upon heating, in alcohol and gasoline, in the cold – in benzene and glacial acetic acid. Crystallized from glacial acetic acid as colorless platelets, m.p. 263° at 23mm. Yield was 0.6 g (31% of theory).

Found %: Br 17.95, 17.96. $C_{26}H_{20}ONBr$. Calculated %: Br 18.08.

3,3-Bis-(3-methoxyphenyl)-6,7-benzhydroxyindole. 30 ml of concentrated sulfuric acid was added to a solution of 3 g of the 3,3-dimethoxybenzylic acid of α-naphthalide in glacial acetic acid. Insoluble in water, poorly so in alcohol; soluble in acetic acid and toluene with heating Colorless, fine needles (from acetic acid) with m.p. 200.5-203°. 1.8 g was obtained (62.7 of theory).

Found %: N 3.78, 3.62. $C_{26}H_{21}O_{3}N$. Calculated %: N 3.54.

SUMMARY

1. In accordance with the mechanism of intramolecular condensation of hydroxycarboxylic acid arylamides, a method, based upon the ability of halochromic salts of arylamides to lose their coloration as the result of intramolecular ring closure, has been used to determine 5-membered heterocyclic closure.

2. It has been established that the rate of 5-membered ring closure for compounds of the $ArNHCOC(OH)Ar'_2$ type is determined both by the nature of the substituting groups and by their position in Ar'. Electron-accepting constituents intensify the electrophilic nature of the carbonium carbon of the halochromic cation of an arylamide and accelerate ring closure; groups with converse action decrease the electrophilic nature of the carbonium carbon and decrease the reaction rate. From the point of view of substituent position, the rate of ring closure takes the order: m > o > p.

3. The effect of steric hindrance upon ring closure has been studied, using as the example o-tolyl and dimesitylglycolic acid anilides. It has also been determined in this study that arylamides in which all four ortho positions of the phenyl radicals attached to the carbinol carbon fail to undergo condensation reaction because of steric hindrance.

4. The rate of 5-membered ring closure has been studied for the α- and β-naphthalides of 4,4'-dimethoxybenzylic acid and also for α,β- and β,β-condensations. It has been determined in this case that the ring closes 4 times more rapidly for the α-naphthalide of 4,4'-dimethoxybenzylic acid than for the β-isomer. With α,β- and β,β condensations, the ring closes at practically the same speed. An explanation for these facts has been given.

5. A number of arylamides of α-hydroxycarboxylic acids, derivatives of 3,3-diarylhydroxyindole, and other compounds not described in the literature, have been synthesized and their properties studied.

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RESEARCH IN THE FIELD OF QUINONES

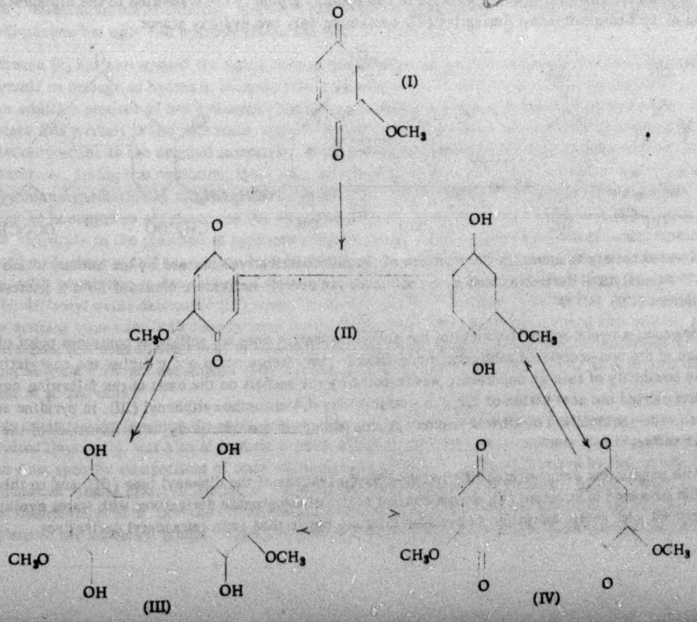
IV. METHOXYQUINONE CONVERSION UNDER THE INFLUENCE OF ACIDS

I. S. Ioffe and A. F. Sukhina

A method is widely used for synthesizing various chloroquinones, consisting in the treatment of quinone with hydrochloric acid, followed by subsequent oxidation of the resulting addition product, which, in one of its tautomeric forms, represents the corresponding chlorohydroquinone. Thus, for example, the chloroquinone is synthesized according to such method, starting with p-benzoquinone. However, this method is unsuitable for the synthesis of chloromethoxyquinones [1], since the methoxyquinone, in the presence of acids, among them hydrochloric, forms a condensation product of two molecules, which separates in the form of violet-blue needle crystals.

Experiments by the authors have demonstrated that this blue substance can be obtained in quantitative yield very smoothly from the methoxyquinone by addition of hydrochloric or sulfuric acid to a dilute aqueous acetate solution of the methoxyquinone.

Erdtman [2] assumed that the blue substance forms as a result of the condensation of two molecules of methoxyquinone (I) or of methoxyquinone and methoxyhydroquinone, with the appearance of a diphenyl bond in the p-position to the methoxyl groups, and represents the intramolecular quinhydrone (II). Indeed, upon reduction of the blue substance, a leuco compound was obtained, from which, after demethylation, there resulted the already described 2,4,5,2',4',5'-hexahydroxydiphenyl. Hence it follows that the indicated leuco compound represents 2,5,2',5'-tetrahydroxy-4,4'-dimethoxydiphenyl (III), and that the intramolecular quinhydrone resulting from it by moderate oxidation has the structure (II). However, upon treating the leuco compound (III), or the blue substance (II) with strong oxidants, for example with chromic acid, there results yellow dimethoxydiquinone (IV).

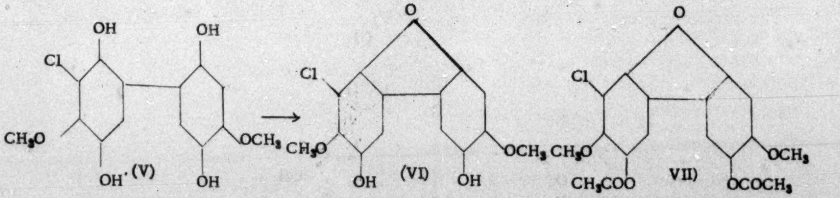


Acid condensation of methoxyquinone is specific for this compound and is conditioned by the effect of the methoxy group. Under analogous conditions such a reaction does not go with either non-substituted p-benzoquinone or its derivatives which contain other substituents.

The possibility came to mind that this reaction ability of methoxyquinone might be used for deriving various unsymmetrical derivatives of diphenyl, through the condensation of methoxyquinone with phenols. However, experiments have not confirmed this assumption. Upon adding hydrochloric acid to a dilute acetate solution of methoxyquinone with phenol, guaicol or hydroquinone, in equimolecular mixture, a pure precipitate of the blue intramolecular quinhydrone (II) resulted in all cases, in amounts corresponding to the weighed methoxyquinone portions used in the reaction. This condensation proceeded only slightly more rapidly in the presence of hydroquinone. It follows from the given experiments that the condensation in question is specific for methoxyquinone, and is conditioned by the combined effect of the methoxyl group and quinoid group.

The author's investigation has demonstrated, however, that the interaction of methoxyquinone with hydrochloric acid is not limited to formation of the blue substance (II). Along with it, some colorless substance is also formed, which, in distinction to compound (II), dissolves in acetic acid and alcohol, separating from these solvents, upon crystallization, as fine, white, needle crystals, melting sharply at 230-231°. This new substance contained chlorine. The author observed that the quantity of colorless chlorine-containing compounds increased both with increased treatment time of the methoxyquinone with hydrochloric acid, and with increased hydrochloric acid concentration; at the same time, the quantity of blue substance (II) decreased accordingly. Under the determined conditions the chloroderivative resulted as the principal reaction product. It follows from these observations that this colorless substance forms not as a result of direct interaction of hydrochloric acid with methoxyquinone, but rather represents an interaction product between hydrochloric acid and the intermediate-forming blue compound (II). In fact, upon shaking a suspension of the earlier prepared and crystallized compound (II) with concentrated sulfuric acid, the blue crystalline precipitate gradually transformed into colorless crystals, which, after purification, melted at 230-231°. Such transformation proceeds much more rapidly and quantitatively upon adding concentrated hydrochloric acid to a boiling suspension of the blue compound (II) in acetic acid.

It was most logical to assume that the chloroderivative obtained by the authors forms as the result of hydrogen chloride addition to intramolecular quinhydrone (II) at the expense of its quinoid radical, and that it represents 3-chloro-2,5,2',5'-tetrahydroxy-4,4'-dimethoxydiphenyl (V). However, quantitative acetylation in pyridine solution has shown that two and not four hydroxy groups are present. In the tetrahydroxydiphenyl derivative (V), it is indeed possible to close the furane ring at the expense of two hydroxy groups in the o-position to the diphenyl bond, with formation of the hydroxydiphenyl derivative (VI) containing only two hydroxy groups.



It was necessary to ascertain the structure of the chloroderivative obtained by the authors which melted at 230-231°. As analytical determinations have indicated, the acetyl derivative obtained from it possessed a cyclic oxide structure (VII).

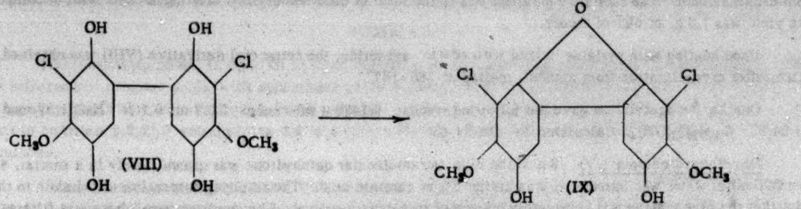
However, a cyclic oxide structure for the acetyl derivative does not suffice as complete proof of identity of structure of the non-acetylated substance, since furane ring closure could occur during the acetylating process. The possibility of such an occurrence was rejected by the authors on the basis of the following experiments. The authors carried out acetylation of 2,5,2',5'-tetrahydroxy-4,4'-dimethoxydiphenyl (III), in pyridine solution. Thereupon, the acetylation of all four hydroxy groups proceeded quantitatively, with formation of the tetraacetyl derivative.

This experiment demonstrated that tetrahydroxyderivatives of the diphenyl type (III), and to this also belongs the substance of structure (V), do not convert to the diphenyloxide derivatives with water evolution, upon treatment with acetic anhydride in pyridine solution, but instead form tetraacetyl derivatives.

It follows from what has been stated above that the colorless chloro-derivative obtained by interaction of the blue quinhydrone (II) with hydrochloric acid contains the oxide ring and has the structure (VI) even before the acetylation. Direct and final proof of this fact was given by determination of active hydrogen (according to Tserevitinov-Chugaev), which indicated the presence of only two hydroxyl groups in the given compound. Confirmation of such a structure can be seen from the fact that the given substance also gave a stable alkaline solution, from which, upon acidification, the substance was isolated in unchanged form. At the same time, all compounds of the type (III) structure, i.e. containing two hydroquinone groupings, oxidize very readily.

Thus, the authors' investigation has indicated that upon interaction of the blue quinhydrone (II) with hydrochloric acid, along with hydrogen chloride addition to the quinoid ring, there also proceeds closure of the oxide ring of the intermediate diphenyl derivative [V] under the effect of hydrochloric acid, with formation of the 3-chloro-5,5'-dihyroxy-4,4'-dimethoxy oxide of diphenyl (VI) as the final product.

During the progress of these works, the authors decided to study also interaction of the corresponding diquinone (VI) with hydrochloric acid. The authors surmised that two hydrogen chloride molecules could be added to this compound containing two quinoid groupings, and that oxide ring closure would be possible for the intermediate diphenyl derivative (VIII) formed, with resulting conversion to the 3,3'-dichloro-5,5'-dihydroxy-4,4'-dimethoxyoxide of diphenyl (IX).



The experiments confirmed our assumptions. Upon addition of concentrated hydrochloric acid to a boiling solution of dimethoxydiquinone (IV) in acetic acid, a colorless precipitate resulted from the solution, which, after crystallization, melted at 235-236°. The acetyl derivative crystallized in the form of colorless needles, melting at 252-253°. Determination of chlorine, methoxyl and hydroxyl groups confirmed that the substance obtained from dimethoxydiquinone has only two hydroxy groups and is of the structure (IX).

Erdtman [2] has also studied the interaction of dimethoxyquinone with hydrochloric acid. However, he limited himself to passage of hydrogen chloride through a solution of dimethoxydiquinone in chloroform, and obtained an addition product of two hydrogen chloride molecules to the dimethoxydiquinone molecule. Erdtman did not isolate this product in the pure state, since it proved to be so unstable that attempts to crystallize it resulted in decomposition to the original materials. This product also decomposed upon heating with acetic anhydride However, during this operation, there was, nonetheless, a small yield of new substance melting at 253°, to which Erdtman hypothetically attributed the structure (IX). On the basis of the authors' investigations, such a structure can be accepted as accurate, and the formation of such a product can be understood, since upon heating with acetic anhydride in the presence of hydrogen chloride (resulting from decomposition of larger amounts of addition products), there should take place both formation of the diphenyl derivative (VIII) and closure of the furane ring, with conversion to derivatives of diphenyl oxide (IX); the latter acetylates to form the diacetyl derivative. The diphenyl oxide derivative (IX) results in almost quantitative yield upon shaking dimethoxydiquinone (IV) in acetate suspension with concentrated hydrochloric acid. The precipitate was at first yellow, acquiring a green shade, and then through blue to colorless. In distinction to the addition product described by Erdtman, the resulting substance did not decompose upon heating, and crystallized from 80% acetic acid to form colorless needles with m.p. 235-236°.

This investigation in which the main purpose was a study of methoxyquinone transformations in the presence of hydrochloric acid, was also of interest to the authors for another reason, namely that the authors were able to carry out specific comparisons of these conversions with acid conversions observed by the authors for methoxyfuchsones. Under effect of the latter, fuchsone derivatives containing methoxyl groups converted, in the presence of hydrochloric acid into the corresponding fluorene derivatives; here the aromatic radicals added in the p-positions to the methoxyl groups. Thus, the fluorene derivatives resulted from dimethoxybenzaurine [3].

For a large number of quinones, the methoxyl groups impart to such compounds containing them distinctive properties. In particular there is the ability of methoxyquinone to form, in the presence of acids, condensation products of two molecules with a compound containing aromatic nuclei in the p-positions to the methoxyl groups. A comparison of this reaction with the above-described reaction of methoxyfuchsone acid conversions has indicated that both reactions are relative and are conditioned by the peculiar effect of methoxyl groups.

EXPERIMENTAL

Synthesis of condensation products with a diphenyl structure from methoxyquinone. Intramolecular quinhydrone (II). 10 g of methoxyquinone (I) was dissolved with heating in 100 ml of glacial acetic acid and the resulting solution poured into 2 liters of 1% hydrochloric acid. A blue precipitate gradually began to form from the solution. After standing for 48 hours, the resulting precipitate was filtered off, washed with water and dried. The yield was 9.5 g or 95% of theory. The resulting precipitate melted at 230° and after recrystallization from pyridine, melted at 238°. This compound was almost insoluble in water and alcohol, and very poorly soluble in acetic acid.

2,5,2',5'-Tetrahydroxy-4,4'-dimethoxydiphenyl (III). 3 g of the blue intramolecular quinhydrone was introduced into 10 ml of acetic acid, and to the suspension was added 3 g of zinc dust, and the mixture heated to complete dissolution of the blue precipitate, and decoloration of the solution. The latter was filtered and the filtrate added to 50 ml of water containing several drops of sodium bisulfate. The resulting precipitate was filtered and crystallized from dilute alcohol. The substance obtained was in the form of colorless crystals melting at 210° with decomposition. The yield was 1.8 g, or 60% of theory.

Upon heating with pyridine mixed with acetic anhydride, the tetracetyl derivative (VIII) was obtained, which, after crystallization from alcohol, melted at 186-187°.

Qualitative acetylation gave the following results: 0.1486 g substance: 21.7 ml 0.1 N NaOH. Found % OH 24.82. $C_{14}H_{10}O_2(OH)_4$. Calculated % OH 24.45.

Dimethoxydiquinone (IV). 3 g of the blue intramolecular quinhydrone was ground finely in a mortar, and then 300 ml of water was introduced, containing 3 g of chromic acid. The resulting suspension was shaken to the point that the blue residue was completely converted to a canary-yellow. The resulting precipitate was filtered off, washed with water and dried. The yield was quantitative. The reaction product melted at 205-207°. After crystallization from acetic acid, it resulted in yellow needles with an m.p. of 212-214°.

5,5'-Dihydroxy-4,4'-dimethoxy-3-chlorooxide of diphenyl (VI). 1) One gram of methoxyquinone was dissolved in 10 ml of acetic acid and to the resulting solution 20 ml of concentrated hydrochloric acid was added. A colorless product precipitated out slowly in crystalline form. After holding for 48 hours, the resulting mixture was poured into 100 ml of water, the precipitate formed filtered off, washed with water and dried. The yield was 0.8 g, or 75% of theory.

2) 3 g of the blue substance was suspended in 30 ml of acetic acid, to the suspension added 10 ml of concentrated hydrochloric acid, and the mixture heated with stirring on a boiling water bath. At 60-70° the precipitate was already decolorized, acquiring a light-gray color. The suspension so formed was poured into 150 ml of hot water and after cooling the precipitate was filtered off, washed and dried. The yield was 3 g, or 95% of theory.

The substance obtained in this manner melted at 215-220°. After crystallization from acetic acid, colorless needles resulted, with m.p. 230-231°.

The substance was poorly soluble in water, moderately so in alcohol and glacial acetic acid; soluble in aqueous alkali, forming a stable solution, upon acidification of which there separated out the unchanged product. Melted at 230-231°. It formed the acetyl derivative upon heating with pyridine and acetic anhydride mixture, which, after crystallization from acetic acid, melted at 220-221°.

The non-acetylated substance.

0.2916, 0.2450 g substance: 20.2, 16.5 ml 0.1 N NaOH. 0.1022, 0.1075 g substance: 16.2, 15.6 ml CH_4. 0.1002 g substance: 0.1548 g AgI. Found % OH 11.77, 11.45, 12.1, 11.1; OCH_3 20.39. $C_{15}H_{15}O_4Cl$. Calculated % OH 11.55; OCH_3 21.05.

The acetyl derivative.

0.1271, 0.1230 g substance: 0.1588, 0.1557 g AgI. Found % OCH_3 16.52, 16.78. $C_{19}H_{19}O_6Cl$. Calculated % OCH_3 16.4

5,5'-Dihydroxy-4,4'-dimethoxy-3,3'-dichlorooxide of diphenyl (IX). 5 g of dimethoxydiquinone was introduced into 25 ml of glacial acetic acid, and to the boiling suspension 25 ml of concentrated hydrochloric acid was added, after which all of the mixture was brought to boiling. Thereupon a light-gray reaction product separated. 100 ml of hot water was added and after cooling was filtered, washed with water and dried. The yield was 4.8 g, or 85% of theory. The crude product melted at 220-225°. After crystallization from acetic acid – colorless needles with m.p. 235-236°.

The substance was poorly soluble in water. It crystallized from alcohol and acetic acid. It was soluble in alkali. Upon acidification of the alkaline solution, it separated in unaltered form. Melting point 235-236°
It formed the acetyl derivative upon heating with pyridine and acetic anhydride mixture, which, after recrystallization from acetic acid resulted as colorless needles, m.p. 252-253°.

Non-acetylated substance.

0.2238, 0.2422 g substance: 13.7, 15.1 ml 0.1 N NaOH. 0.1040, 0.1243 g substance: 13.8, 17.0 ml CH_4. 0.1194, 0.1510 g substance: 0.1054, 0.1296 g AgCl. Found %: OH 10.45, 10.52, 10.1, 10.5; Cl 21.44, 21.25. $C_{14}H_{10}O_6Cl_2$. Calculated %: OH 10.37; Cl 21.6.

The acetyl derivative.

0.1012 g substance; 0.1155 g AgI. Found %: OCH_3 15.01. $C_{18}H_{14}O_7Cl_2$. Calculated %: OCH_3 15.08.

SUMMARY

The methoxyquinone, in contrast to other quinones, forms a condensation product of two molecules under the influence of mineral acids, with appearance of the diphenyl bond in the p-position to the methoxyl groups. This compound is blue in color, and is found to be the intramolecular quinhydrone, which, upon reduction, converts to colorless 2,5,2',5'-tetrahydroxy-4,4'-dimethoxy diphenyl, and upon oxidation, to the yellow dimethoxydiquinone.

Upon interacting methoxyquinone with concentrated hydrochloric acid, the reaction is not limited to formation of the blue intramolecular quinhydrone. To the latter a molecule of hydrogen chloride is added at the expense of the quinoid group, and with 3-chloro-2,5,2',5'-tetrahydroxy-4,4'-dimethoxydiphenyl, the furane ring is closed under the influence of hydrochloric acid, with water evolution and formation of the corresponding colorless diphenyl oxide derivative, m.p. 230-231° (diacetyl derivative, m.p. 220-221°).

In an analogous fashion, upon treating dimethoxydiquinone with hydrochloric acid, two hydrogen chloride molecules add to the former, with intermediate formation of 3,3'-dichloro-2,5,2',5'-tetrahydroxy-4,4'-dimethoxy diphenyl, under which reaction conditions closure of the furane ring occurs, with conversion to the corresponding dichloroderivative of diphenyloxide with m.p. 235-236° (diacetyl derivative, m.p. 252-253°).

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* See Consultants Bureau Translation, page 307.
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[illegible] or 85% of theory. The [illegible] needles with m.p. 236-238°.

The substance was poorly soluble in water [illegible] it formed the acetyl derivative [illegible] acetic acid [illegible]

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SUMMARY

The [illegible]oxyphenol, in contrast to other [illegible], forms a [illegible] under the influence of mineral acids, with [illegible] of the [illegible] converts to [illegible] 2,6,2',6'-tetra[illegible]-4,4'-[illegible] diphenyl [illegible]

[illegible] formation of the blue [illegible] of the [illegible] group [illegible] ring is closed under the influence of [illegible] diphenyl [illegible] derivative, m.p. 230-232° [illegible]

In an analogous [illegible] diphenyl [illegible] of diphenylene with m.p. [illegible]

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THERMAL DECOMPOSITION OF BENZOYL PEROXIDE IN CARBON TETRACHLORIDE-METHYL ALCOHOL MIXTURE

G. A. Razuvaev, B. N. Moryganov and V. A. Stepushkina

Carbon tetrachloride, previously considered an almost inactive compound, has been found capable of adding to olefins in the presence of peroxides and light [1]. It has been considered usually that the action of ultraviolet light and benzoyl peroxide or acetyl peroxide produces analogous reactions. However, A. E. Borisov has been able to demonstrate that carbon tetrachloride and diphenylmercury reactions take a different course of action under the influence of acetyl peroxide as compared with the same reaction proceeding under the influence of ultraviolet light. In the first case benzotrichloride is formed, i.e., interaction of the phenyl radical with the CCl_3 radical occurs, and in the second case just dimerization, leading to hexachloroethane.

The authors have indicated a different direction for the reaction of carbon tetrachloride with alcohols under the influence of temperature and ultraviolet light [3]. Upon heating carbon tetrachloride with methyl alcohol to 200-210°, there proceeds formation of chloroform, formaldehyde and HCl, but under the influence of ultraviolet light, CCl_3-radicals give hexachloroethane.

It was of interest to clarify whether or not benzoyl peroxide will initiate reaction of carbon tetrachloride with alcohols, and if this reaction goes, whether it will follow the direction of thermal reaction or photoreaction. With thermal decomposition of benzoyl peroxide in carbon tetrachloride and methyl alcohol mixture, the following can be hypothesized.

1. Benzoyl peroxide will react only with carbon tetrachloride:

$$(C_6H_5COO)_2 + CCl_4 \rightarrow C_6H_5Cl + C_2Cl_6 + \text{phthalic acid} + CO_2 \qquad (1)$$

2. Benzoyl peroxide will react only with methyl alcohol.

3. Benzoyl peroxide will initiate reaction between carbon tetrachloride and methyl alcohol, as indicated above [3].

It has been found that benzoyl peroxide reaction with alcohols is almost non-existant in the literature: the decomposition kinetics of benzoyl peroxide in alcohol without the evolution of reaction product [4] has been studied, and only the reaction of benzoyl peroxide with isobutyl alcohol has been studied in some detail [5].

The authors therefore, set up experiments on the decomposition of benzoyl peroxide in methyl alcohol over a wide temperature range (from 70 to 150°), and have determined that reaction proceeds with formation chiefly of benzoic acid, methylbenzoate and formaldehyde [2]. Reaction (3) to give benzene and CO_2 proceeded, but to a lesser degree.

$$(C_6H_5COO)_2 + CH_3OH \rightarrow 2C_6H_5COOH + CH_2O; \qquad (2)$$

$$(C_6H_5COO)_2 + CH_3OH \rightarrow C_6H_6 + CO_2 + C_6H_5COOH + CH_2O. \qquad (3)$$

In carrying out experiments on initiation of the carbon tetrachloride and methyl alcohol reaction by benzoyl peroxide, there resulted chloroform hexachloroethane, formaldehyde, HCl, benzoic acid, methylbenzoate, phthalic acid and CO_2.

The formation of hexachloroethane and phthalic acid attested to the fact that benzoyl peroxide reacts with carbon tetrachloride.

Isolation of benzoic acid, methyl benzoate and formaldehyde indicated that the benzoyl peroxide reacted with methyl alcohol.

It may be said, however, that benzoyl peroxide initiated the reaction between carbon tetrachloride and methyl alcohol, which is indicated by evolution of HCl and separation of chloroform. It can be seen definitely, therefore, that the reaction, to some degree, proceeds according to equation (4):

$$CCl_4 + CH_3OH \rightarrow HCl + CHCl_3 + CH_2O. \tag{4}$$

EXPERIMENTAL

I. Thermal decomposition of benzoyl peroxide in methyl alcohol. Heating of the components was carried out both in a flask with condenser, and in sealed tubes at higher temperatures.*

a) 79 g (100 ml) of methyl alcohol and 10 g of benzoyl peroxide were heated for 20 hours with a reflux condenser. The carbon dioxide evolved was absorbed in traps with 40% potassium hydroxide solution. 0.72 g of carbon dioxide was evolved (0.40 mole for 1 mole of the peroxide decomposed). The reaction mixture was distilled, and the fraction distilled off diluted with water. The small amount of benzene that separated was extracted with carbon tetrachloride and nitrated. m-Dinitrobenzene resulted, with m.p. 90°; a mixed sample with known m-dinitrobenzene did not give depression. 0.11 g of m-dinitrobenzene was obtained, which corresponded to 0.05 g of benzene, or 0.01 mole for 1 mole of peroxide decomposed. Formaldehyde content was determined in the aqueous-alcoholic solution by precipitation of the dimedonic derivative; 0.005 g of formaldehyde was found, or 0.004 mole for 1 mole of peroxide. The dimedonic derivative of formaldehyde melted at 187°; a mixed sample with known sample of dimedonic derivative did not give depression. Benzoic acid was determined by titration: 5.84 g was obtained, or 1.16 mole for 1 mole of the peroxide decomposed. A portion of the benzoic acid converted into the methyl ester under the experimental conditions. To determine the total amount of benzoic acid, saponification was carried out on a separate sample, which gave an ester content of 3.15 g or 0.56 mole for 1 mole of peroxide. Thus, the total quantity of benzoic acid constituted 1.72 mole for 1 mole of peroxide decomposed. Benzoic acid melted at 121°; a mixed sample with pure benzoic acid did not give depression.

b) A weighed portion of benzoyl peroxide (3 g) was heated in a sealed tube with methyl alcohol (20 ml) at 120-150° for 20 hours. Benzoic acid determination was carried out by titration. 1.64 g of free benzoic acid was obtained (1.07 mole for 1 mole of peroxide decomposed). Determination of methylbenzoate was carried out by saponification. 0.76 g of methylbenzoate resulted (0.45 mole for 1 mole of peroxide decomposed). The total quantity of benzoic acid was 2.38 g (1.58 mole for 1 mole of peroxide), m.p. 121°; a sample mixed with known benzoic acid did not show depression.

After distilling off the methyl alcohol, benzene was extracted from the distilled fraction, and carbon tetrachloride after dilution with water. m-Dinitrobenzene resulted from nitration, with an m.p. of 90°; a sample mixed with known m-dinitrobenzene did not evidence depression. 0.095 g of m-dinitrobenzene was found, which corresponded to 0.044 g of benzene or 0.04 mole for 1 mole of peroxide decomposed. Formaldehyde was determined in the aqueous-alcoholic solution by precipitation of the dimedonic derivative; 0.005 g or 0.01 mole for 1 mole of peroxide was found. The resulting product melted at 187°; a sample mixed with known dimedonic derivative of formaldehyde did not show depression.

II. Thermal decomposition of benzoyl peroxide in carbon tetrachloride-methyl alcohol mixture. Reaction was carried out in a round-bottomed flask with ground-glass reflux condenser. The reaction mixture was heated on a water bath for 40 hours. In each experiment 50 g of benzoyl peroxide was decomposed in equimolecular amounts of carbon tetrachloride (154 g), and methyl alcohol (32 g). Long before termination of heating, the reaction mixture separated into two layers: upper – aqueous, and lower – nonaqueous. Gases formed during the reaction were absorbed in traps by 40% KOH solution. The hydrochloric acid content of traps 0.09 g (0.01 mole for 1 mole of peroxide decomposed), was gravimetrically determined. The quantity of CO_2 – 7.83 g (0.83 mole for 1 mole of peroxide decomposed) – was determined by difference.

The non-aqueous layer was washed with distilled water to remove methyl alcohol and other water-soluble substances, the wash waters being added to the aqueous layer and the volume of the mixture measured. The upper aqueous layer had an acid reaction, the non-aqueous layer a neutral reaction.

The aqueous layer contained formaldehyde, methylal and hydrochloric acid. The formaldehyde was determined by precipitation of the dimedonic derivative – 0.42 g (0.07 mole for 1 mole of peroxide decomposed). The quantity of formaldehyde in the free state, and the total quantity of formaldehyde were determined. For determination of the total quantity of formaldehyde, the methylal contained in the aqueous layer was split, by heating the latter in dilute hydrochloric acid with a reflux. 0.45 g of methylal was found (0.03 mole for 1 mole of peroxide decomposed). The dimedonic derivative of formaldehyde melted at 187°; the sample mixed with a known sample of the dimedonic derivative did not show depression. The quantity of hydrochloric acid in the aqueous layer was 3.19 g (0.42 mole for 1 mole of the peroxide decomposed) —determined by titration.

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* B. I. Liogonky participated in this work.

The non-aqueous layer contained carbon tetrachloride, formaldehyde, methylal, chloroform, hexachloroethane, benzoic acid, methylbenzoate and phthalic acid. To split methylal into alcohol and formaldehyde, the non-aqueous layer was heated with dilute hydrochloric acid on a reflux. 3.71 g of methylal, or 0.24 mole for 1 mole of peroxide decomposed, was found. Formaldehyde was determined in the water-acid solution after rupture of the methylal by precipitation of the dimedonic derivative. 1.48 g, or 0.24 mole for 1 mole of the peroxide decomposed.

By distilling on a fractionating column, a fraction was isolated with a b.p. of 64.5-66°; d_4^{20} 1.5094; n_D^{20} 1.4470. Chloroform was quantitatively determined in it by heating with aniline and alkali [6]. 2.46 g of chloroform resulted, or 0.09 mole for 1 mole of peroxide decomposed. After distilling off the carbon tetrachloride and chloroform, the residue was alkalized and steam distilled. From the non-aqueous distillate layer containing carbon tetrachloride, there was isolated methylbenzoate and hexachloroethane. The non-aqueous layer was fractionated. After distilling off the fraction with b.p. 85-141°, hexachloroethane was isolated from the residue with m.p. 186-187°; a sample mixed with hexachloroethane did not show depression.

Methylbenzoate contained in the filtrate after separation of hexachloroethane was saponified to benzoic acid. 2.92 g (0.1 mole for 1 mole of peroxide decomposed) was found. Hexachloroethane was isolated from the alkaline-alcoholic solution after saponification of the methylbenzoate, and was added to that made earlier in the corresponding experiment. The total quantity of hexachloroethane was 4.30 g (0.09 mole for 1 mole of the peroxide decomposed).

Benzoic acid was isolated by acidification of the alkaline-alcoholic solution, and the hexachloroethane separated melted at 121°; the mixed sample did not show depression.

After termination of the steam distillation, from the alkaline solution in the distilling flask there was isolated a small amount of resin, after which the solution was acidified with dilute hydrochloric acid. A mixture of benzoic and phthalic acids was isolated. Benzoic acid isolated from the mixture melted at 121°; a mixed sample with pure benzoic acid did not show depression. o-Phthalic acid was identified by the fluorescein reaction with resorcinol. Benzoic and phthalic acids were determined by titration. 22.65 g (0.9 mole for 1 mole of peroxide decomposed) of benzoic acid and 1.1 g (0.03 mole for 1 mole of peroxide decomposed) were found.

SUMMARY

1. Upon heating with methyl alcohol, benzoyl peroxide reacts with formation of benzoic acid, formaldehyde, benzene and carbon dioxide.

2. Upon heating a mixture of methyl alcohol and carbon tetrachloride in the presence of benzoyl peroxide, there proceeds reaction of the latter with both components. Moreover, a reaction between carbon tetrachloride and methyl alcohol is initiated by the peroxide, with formation of chloroform, formaldehyde and HCl. The direction of the initiated reaction corresponds to the thermal reaction between methyl alcohol and carbon tetrachloride.

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determination of the total number of [illegible] by heating the [illegible] with [illegible] amide decomposed). The dinitrophenylhydrazone [illegible] sample of the dinitrophenylhydrazine derivative did not show depression. [illegible] was 0.?8 g (0.14 mole for 1 mole of the parent [illegible]).

The non-acidic layer contained carbon tetrachloride [illegible] layer was heated with dilute hydrochloric acid [illegible] decomposed, was found. [illegible] condensation of the [illegible]

By distilling [illegible] [illegible]

Merely [illegible] observed in the [illegible]

[illegible] acid was isolated by [illegible]

After [illegible] ([illegible] mole for 1 mole of [illegible]).

1. Upon heating [illegible] [illegible]

2. Upon heating a mixture of methyl [illegible]

LITERATURE CITED

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[2] A. D. [illegible]

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THERMAL DECOMPOSITION OF BENZOYL PEROXIDE IN SOLVENT MIXTURES: BENZENE AND NITROBENZENE AND NITROBENZENE AND CARBON TETRACHLORIDE

G. A. Razuvaev, B. N. Moryganov and V. A. Stepushkina

It is quite convenient to use benzoyl peroxide for investigation of free radical reactions in the liquid phase, which, as is known from the works of S. Medvedev and co-workers, decomposes into the phenyl- and hydroxybenzoyl radicals [1]. There has appeared lately a number of works devoted to reactions of benzoyl peroxide. It appeared to be of interest to the authors to carry out an investigation of the peroxide decomposition in a mixture of two different solvents in order to determine: 1) whether interaction of peroxide will occur with both components of the mixture, or only one, and 2) whether the secondary radicals forming from the solvents will react with one another. Insofar as the authors are aware, there is practically no such type of work to be found in the literature. For this purpose we have investigated two systems: 1) benzene and nitrobenzene, and 2) nitrobenzene and carbon tetrachloride. It is known [2] that when benzoyl peroxide is heated in benzene, reaction occurs, which is expressed by the following summary equation:

$$(C_6H_5COO)_2 + C_6H_6 \rightarrow C_6H_5COOH + CO_2 + C_6H_5C_6H_5, \qquad (1)$$

and upon decomposition in nitrobenzene [3]:

$$(C_6H_5COO)_2 + C_6H_5NO_2 \rightarrow C_6H_5COOH + CO_2 + C_6H_5C_6H_4NO_2. \qquad (2)$$

There is indication [4] that in the latter case small amounts of diphenyl are obtained. Formation of the latter may be explained by reaction of benzoyl peroxide with benzene, which appears in the reaction mixture in the nature of a side product of the peroxide. During the reaction course in benzene and nitrophenol mixture, which were taken in a 1:1 mole ratio, the following products resulted: CO_2, benzoic acid, diphenyl and nitrodiphenyls. Thus, it can be seen that interaction of benzoyl peroxide with benzene and nitrobenzene proceeded simultaneously. From the mole ratio of diphenyl to nitrodiphenyls (9:7) it can be seen that the peroxide reacted more readily with benzene.

The second question — whether interaction of secondary free radicals with one another occurred — cannot be answered with the given system, since the final products would be the same in such a reaction. A second system might give an answer to this problem. When benzoyl peroxide interacts with carbon tetrachloride [5], the following reaction proceeds:

$$(C_6H_5COO)_2 + CCl_4 \rightarrow C_6H_5COOCCl_3 + C_6H_5Cl + CO_2; \qquad (3)$$

$$C_6H_5COOCCl_3 \rightarrow Cl_3CC_6H_4COOH. \qquad (4)$$

Moreover, hexachloroethane results as the result of dimerization of CCl_3-radicals. The authors obtained the following reaction products: HCl, chlorobenzene, hexachloroethane, nitrodiphenyl, benzoic acid, phthalic acid and also CO_2. Hence, the benzoyl peroxide reacted simultaneously with both components of the mixture. From the mole ratio of chlorobenzene to nitrodiphenyl (31:6) it can be seen that the peroxide reacted preferably with carbon tetrachloride rather than with the nitrobenzene.

With free CCl_3- and nitrophenyl-radicals in the system, their combination with one another to form nitrobenzotrichloride could be expected.

$$CCl_3^{\cdot} + O_2NC_6H_4^{\cdot} \rightarrow O_2NC_6H_4CCl_3. \qquad (5)$$

However, the authors were unable to find the indicated compound among the reaction products.

EXPERIMENTAL

I. Thermal decomposition of benzoyl peroxide in benzene and nitrobenzene mixture. The reaction mixture was introduced into a round-bottomed flask equipped with reflux condenser and heated on a water bath. In each experiment 50 g of benzoyl peroxide was decomposed with equimolecular quantities of benzene (78 g) and nitrobenzene (123 g). The carbon dioxide formed during reaction was absorbed in traps containing 40% KOH solution. 13.49 g of CO_2 was found, or 1.48 mole for 1 mole of the peroxide decomposed. Sodium hydroxide solution was added to the reaction products (dark-brown solution) to a weak alkaline reaction, and the mixture was distilled with superheated steam. In the first few liters of distillate, a mixture of benzene and nitrobenzene was collected; in subsequent liters—nitrodiphenyl. The benzene-nitrobenzene mixture (from the distillate) was fractionated and the benzene fraction separated from the nitrobenzene fraction. The nitrobenzene fraction contained diphenyl, for the isolation of which the method of nitrobenzene reduction to aniline by Sn and HCl [4] was used. The diphenyl isolated by this procedure in the amount of 3.06 g (0.09 mole for 1 mole of peroxide decomposed), after recrystallization from alcohol, melted at 68-69°, a mixed sample with pure diphenyl melting at 69°. The nitrodiphenyl distilled with steam, in the amount of 2.93 g, or 0.07 mole for 1 mole of peroxide decomposed, melted at 102-103° before recrystallization. 4-Nitrodiphenyl with m.p. 113° was isolated by recrystallization from methyl alcohol; a sample mixed with pure 4-nitrodiphenyl did not show depression. The residue, after distillation with steam, was acidified with dilute sulfuric acid, the resulting precipitate separated from the solution, dried and sublimed. The sublimed benzoic acid (6.13 g) had an m.p. of 121-121.5°, a sample mixed with pure benzoic acid not giving depression. Upon distilling the reaction products with steam there remained each time in the distilling flask a resin (8.41 g).

II. Thermal decomposition of benzoyl peroxide in nitrobenzene and carbon tetrachloride mixture. Experiments were carried out analogously to the preceding ones. In one experiment, 50 g of benzoyl peroxide was decomposed with equimolecular quantities of carbon tetrachloride (154 g) and nitrobenzene (123 g). The decomposition products (dark brown solution) were alkalized and distilled with superheated steam. From the first few liters of distillate a non-aqueous layer separated, consisting of carbon tetrachloride, chlorobenzene and nitrobenzene mixture, and from subsequent liters—nitrodiphenyls. The carbon tetrachloride, chlorobenzene and nitrobenzene mixture was fractionated, and the carbon tetrachloride, chlorobenzene and nitrobenzene fractions were separated from one another. Upon fractionation of these fractions, a small amount of hexachloroethane with m.p. 186° was isolated; a sample mixed with known hexachloroethane did not show depression.

Chlorobenzene in the amount of 7.82 g, or 0.31 mole for 1 mole of peroxide decomposed, was identified by conversion into p-nitrochlorobenzene by nitration of the chlorobenzene fraction. p-Nitrochlorobenzene recrystallized from methyl alcohol melted at 82°; a sample mixed with known p-nitrochlorobenzene did not give depression.

From the mixture of reaction products, by steam distillation, nitrodiphenyl in the amount of 2.42 g, or 0.06 mole for 1 mole of peroxide decomposed, was isolated. 4-Nitrodiphenyl, with m.p. 113-114°, resulted on recrystallization from methyl alcohol, a mixed sample with known 4-nitrodiphenyl not showing depression.

The alkaline dark-brown solution in the distilling flask after completion of the steam distillation was separated from the resin formed and acidified with dilute sulfuric acid. The resulting precipitate was purified a second time by dissolution in alkali and precipitation by acid. The resulting mixture of benzoic and phthalic acids was separated by recrystallization. 21.12 g, or 0.84 mole for 1 mole of peroxide decomposed, of benzoic acid was found, and 2.30 g of o-phthalic acid, or 0.07 mole for 1 mole of peroxide decomposed. o-Phthalic acid was qualitatively identified by the fluorescein reaction. Benzoic acid was purified by sublimation, and melted at 121.5°; a sample mixed with known benzoic acid did not evidence depression. Nitrobenzoic acids were not found.

Gases formed in the reaction were absorbed in the traps by 40% KOH solution. The HCl content of the traps was 6.68 g, or 0.88 mole for 1 mole of peroxide, determined quantitatively by the gravimetric procedure. The quantity of CO_2 was determined by difference; 8.8 g, or 0.94 mole for 1 mole of peroxide decomposed, was found.

SUMMARY

1. It has been demonstrated that the phenyl radicals formed upon thermal decomposition of benzoyl peroxide in a benzene-nitrobenzene mixture react with both benzene and nitrobenzene. From the ratio of diphenyl and nitrodiphenyl formed, it can be seen that the phenyl radicals preferentially react with benzene, rather than with nitrobenzene.

2. It has been demonstrated that the phenyl radicals formed upon thermal decomposition of benzoyl peroxide in carbon tetrachloride-nitrobenzene mixture react with both of the components of the mixture. From the chlorobenzene and nitrodiphenyl formed, it may be judged that the phenyl radicals preferentially react with carbon tetrachloride rather than with nitrobenzene.

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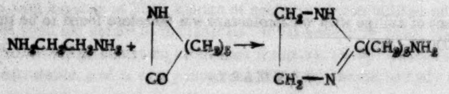
ε-CAPROLACTAM RING OPENING BY ALIPHATIC DICARBOXYLIC ACIDS AND BY AMINES

A. S. Shpitalny, E. A. Meos and K. E. Perepalkin

Some of us have already reported [1] that upon interacting ε-caprolactam with aliphatic dicarboxylic acids, there occurs ε-caprolactam ring opening, with formation of dicarboxylic acids of the $HOOCRCONH(CH_2)_5COOH$ type. The calcium and silver salts of these acids have already been described by the authors.

Since directions in the literature [2] indicated the possibility of rupturing the lactamic bond of ε-caprolactam by amines, the authors made an attempt to obtain interaction products of ε-caprolactam with aniline, hexamethylenediamine and ethylenediamine. The corresponding monoamino and diamino derivatives were formed by coupling aniline and hexamethylenediamine with ε-caprolactam in equimolecular ratios. Interaction of ethylenediamine with ε-caprolactam in the same ratio led to formation of the imidazole derivative.



Those indicated amines which were readily soluble in water, alcohol and ether, failed to separate in crystalline form from the reaction mass.

Since it was shown that the benzoyl derivatives of these compounds crystallize well from alcohol-ether solutions, the authors isolated their benzoyl derivatives. Some of the products were also obtained in the form of picrates and oxalates. It was proved by these experiments that in the polymerization-condensation processes taking place in conversion of ε-caprolactam into the polymer [1], interaction of terminal carboxyl and amino groups of the polymer participate, despite the polycondensation reaction.

It also follows from the above-stated that along with the already known methods of synthesis of imidazole derivatives [3], the latter can be obtained by interaction of ethylenediamine with ε-caprolactam.

EXPERIMENTAL

Synthesis of 2-(ε-aminopentyl)-4,5-dihydroimidazole, a conjugation product of ethylenediamine with ε-caprolactam. 1.88 g of ε-caprolactam and 1 g of ethylenediamine (equimolecular ratios) were heated in a sealed tube for 24 hours at 200° in an oil bath. The ampoule was then opened and the reaction mass heated for another hour under vacuum (8 mm) at 150°. Thus, about 10 g of melt was prepared. The benzoyl derivative of the conjugated product was obtained as follows: 1 g of the melt was dissolved in 100 ml of water; 16 ml of 10% sodium hydroxide solution and 3 ml of benzoyl chloride were added. The mixture was shaken 15 minutes, and the white, flaky precipitate formed was filtered off and recrystallized from alcoholic-ether solution.

The benzoyl derivative dissolved readily in alcohol poorly in water and ether, and had an m.p. of 141°.

Found %: C 72.5, 72.61; H 6.75, 6.67; N 11.46, 11.44. $C_{22}H_{25}O_2N_3$. Calculated %: C 72.72; H 6.88; N 11.57.

The picrate of the conjugation product was obtained from both alcoholic and aqueous solutions. Its melting point was 190-200° (with decomposition).

Found %: N 21.02, 20.80. $C_{20}H_{23}O_{14}N_9$. Calculated %: N 20.58.

The picrate of the conjugation product was isolated from alcoholic solution. Upon recrystallizing from alcoholic-aqueous solution, needle crystals, with m.p. 204-206° (with decomposition) precipitated.

Found %: C 38.60, 38.72; H 6.51, 6.55; N 11.29, 11.3. $C_{12}H_{25}O_{10}N_3$. Calculated %: C 38.81; H 6.73; N 11.32.

The amount of water of crystallization in the salt was determined by drying the air-dried product at 160° to constant weight (about 1 hour).

Found %: H_2O 10.01, 9.97. $C_{12}H_{21}O_8N_3 \cdot 2H_2O$. Calculated %: H_2O 9.70.

Thus, the oxalate of the conjugation product contained 2 moles of oxalic acid and 2 moles of water.

The analyses given above indicated, accordingly, that the conjugation product of ethylenediamine and ε-caprolactam represented 2-(ε-aminopentyl)-4,5-dihydroimidazole.

Synthesis of N-(ζ-aminohexyl)-amide and ε-aminocapronic acid, a conjugation product of hexamethylenediamine with ε-caprolactam. The given conjugation product and its benzoyl derivative was synthesized in exactly the same manner as the ethylenediamine derivatives described above. The benzoyl derivative of the conjugation product had an m.p. of 118°, soluble in alcohol, insoluble in water and ether.

Found %: C 71.12, 71.2; H 7.9, 8.05; N 9.75, 9.93. $C_{26}H_{35}O_3N_3$. Calculated %: C 71.39; H 8.01; N 9.61.

Thus, the conjugation product of hexamethylenediamine and ε-caprolactam satisfies the formula for the N-(ζ-aminohexyl)-amide of ε-aminocapronic acid $NH_2(CH_2)_6NHCO(CH_2)_5NH_2$.

Synthesis of the N-phenylamide of ε-aminocapronic acid, a conjugation product of aniline with ε-caprolactam. The benzoyl derivative dissolved in alcohol and ether and did not dissolve in water; it was therefore recrystallized from a water-alcohol solution. The benzoyl derivative had an m.p. of 102 - 103°.

Found %: C 73.40, 73.32; H 6.92, 6.85; N 8.89, 9.30. $C_{19}H_{22}O_2N_2$. Calculated %: C 73.55; H 7.09; N 9.03.

The conjugation product of aniline with ε-caprolactam was therefore found to be the N-phenylamide of ε-aminocapronic acid $C_6H_5NHCO(CH_2)_5NH_2$.

SUMMARY

1. The interaction products of aniline, hexamethylenediamine and ethylenediamine with ε-caprolactam, and their benzoyl derivatives, have been synthesized. Some of these products have also been isolated in the form of picrates and oxalates.

2. It has been demonstrated that imidazole derivatives are formed upon interaction of ethylenediamine with ε-caprolactam.

3. Concepts about the character of the reactions which take place during the polymerization-condensation processes involving conversion of ε-caprolactam into the polymer have been given.

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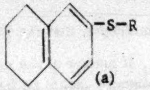
*See Consultants Bureau Translation, p. 1311.

THE SYNTHESIS AND CATALYTIC CONVERSION OF β-THIOTETRALOL, β-TETRALYLNONYLSULFIDE, β-TETRALYLCYCLOHEXYLSULFIDE AND β-TETRALYLMETHYLSULFIDE OVER ALUMINOSILICATE CATALYST

I. N. Tits-Skvortsova and T. A. Danilova

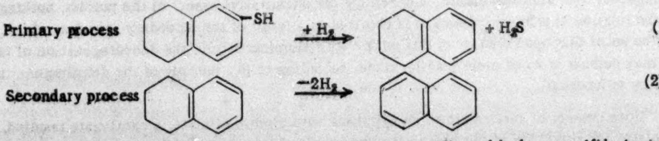
In the works published earlier by the authors [1,2], data are given concerning catalytic conversions over aluminosilicate catalyst of mixed sulfides possessing various structures. Upon the contact of mixed sulfides containing various radicals with catalyst at 300°, rupture of one of the bonds binding sulfur to radicals occurs, and the place of rupture depends upon the nature of the radicals. It has been determined that the bond between the aromatic ring and sulfur is most stable, and in no event does it rupture; however, the bond between sulfur and the naphthene ring is the least stable, and is easily ruptured. It was of interest to study the behavior of those mixed sulfides in which sulfur is bound by one of its valences to a radical composed of a condensed system of aromatic and naphthene rings, which are at two extremes with each other relative to stability of the carbon to sulfur bond. Tetralin, composed of benzene and cyclohexane rings, is such a condensed system.

The purpose of our work was to elucidate whether the hexamethylene ring condensed with the aromatic will effect a rupture of the bond between sulfur and the radicals upon contact of mixed sulfides of the structure (a) with aluminosilicate, and whether in this case the stability of the bond between sulfur and the aromatic ring will be maintained, or whether new mechanisms will appear in the tetralin series.



(a)

Synthesized sulfur compounds were passed over aluminosilicate catalyst at 300° under identical conditions. Upon contact of β-thiotetralol with aluminosilicate, there were isolated tetralin (34% of the catalyzate weight), naphthalene (28%), initial β-thiotetralol (7%). 21% of the sulfur contained in the original thiol was trapped as hydrogen sulfide. A small amount of elementary sulfur was contained in the catalyzate, found by shaking a sample of catalyzate with metallic mercury. On the basis of these data, the processes taking place when β-thiotetralol is catalyzed can be expressed by the following schemes:



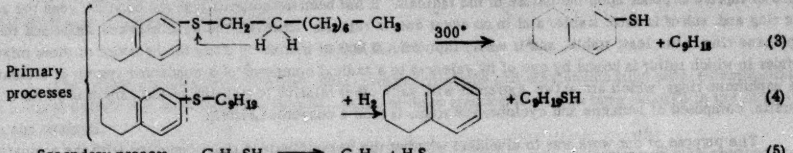
As a result of destructive hydrogenation, β-thiotetralol converts to tetralin and hydrogen sulfide (a similar reaction also occurs with thiophenols [1,2]). Then, as a result of dehydrogenation of tetralin, naphthalene forms. Up to the present time, dehydrogenation of the hexamethylene ring of sulfur compounds under catalytic conditions has not been observed by the authors. According to the literature data [3,4], more probable seems to be the process of isomerization of the hexamethylene ring of tetralin into pentamethylene, with formation of 1- and 2-methylhydroindene mixture. However, the catalyzate did not contain fractions which corresponded in constants to the isomeric liquid methylhydroindenes. To verify the possibility of dehydrogenating tetralin, the latter was passed over aluminosilicate catalyst under conditions of contact with the sulfur compounds. The catalyzate contained only 1.4 % naphthalene, the rest — tetralin; while naphthalene in the amount of 28% of the catalyzate weight was isolated by catalysis of β-thiotetralol. Such a difference in the amount of naphthalene can be explained by the fact that dehydrogenation of tetralin proceeds not under the influence of aluminosilicate alone, but in addition the elementary sulfur appears to be a dehydrogenating agent. To verify this assumption, tetralin was passed over aluminosilicate with sulfur compounds and simultaneously nitrogen and hydrogen sulfide. (The latter decomposed under the influence of aluminosilicate, to form hydrogen and sulfur, the presence of which were proved both in the catalyzate and used catalyst.) The quantity of naphthalene in the catalyzate increased from 1.4 to 4.6 %. This proved the possibility of dehydrogenation of tetralin, but the process proceeded only to a very small extent. The considerably greater quantity of naphthalene obtained in the catalyzate upon contact of β-thiotetralol might possibly be explained by the fact that the tetralin molecule at its moment of formation from β-thiotetralol can more readily undergo dehydrogenation than the already "primed" molecule.

Dehydrogenation of tetralin under the influence of sulfur has been described in the literature [3,5,6]. In the process, which is non-catalytic, the hydrogen evolved combines with sulfur to give hydrogen sulfide. The possibility of this process in the authors' case is confirmed by the absence of hydrogen in the gas evolving upon catalysis of β-thiotetralol: upon catalytic dehydrogenation of tetralin, the gas evolved should have contained hydrogen.

Somehow or other,, a new phenomenon has been observed — dehydrogenation of the hexamethylene ring of tetralin with formation of naphthalene — upon passage of β-thiotetralol over aluminosilicate.

From the catalyzate obtained, there were separated from β-tetralylnonylsulfide: tetralin (27% of the catalyzate weight), nonene-1 (16%), β-thiotetralol (3%), naphthalene (4%), and nonylmercaptan (4%). 19% of the sulfur contained in the original sulfide was trapped as hydrogen sulfide.

It could have been assumed that the following process might proceed upon catalysis of β-tetralylnonylsulfide:

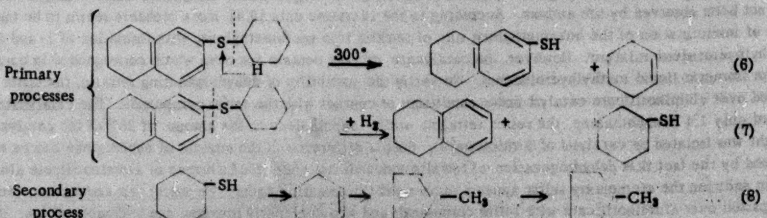


Secondary process $C_9H_{19}SH \longrightarrow C_9H_{18} + H_2S$ (5)

and, moreover, that the secondary processes would proceed according to Equations (1) and (2).

If rupture of the sulfide molecule occurs between the sulfur and the alkyl (Scheme 3), then β-thiotetralol and nonene-1 should be formed; in the case of bond rupture between sulfur and the tetralin radical (Equation 4), tetralin and nonylmercaptan should be formed. But inasmuch as tetralin and nonene may form as the result of secondary processes (Equations 1 and 5*), their presence in the catalyzate is not proof of the accuracy of Equations 3 and 4). The point at which the sulfide molecule ruptures is determined by the thiols which are found to be primary products. All possible compounds foreseen by the above-given equations have been separated from the catalyzate, among them both thiols. Hence, rupture of the β-tetralylnonylsulfide molecule occurred at both valence points of the sulfur — this phenomenon also being observed for the first time upon catalysis of sulfur compounds over aluminosilicate. Concerning the quantitative aspect of the process, nothing can be said, since the relation of primary substances is obscured as a result of the secondary reactions which take place. It should be noted that upon contact of this sulfide with aluminosilicate, the dehydrogenation of tetralin to naphthalene may perhaps proceed more readily, since, according to [6], the role of the dehydrogenating agent may be played by sulfur itself.

Upon contact of β-tetralylcyclohexylsulfide with aluminosilicate, a catalyzate resulted, from which was isolated tetralin (28% of the catalyzate weight), β-thiotetralol (18%), methylcyclopentane (17%), naphthalene (7%), and the initial sulfide (3%). Sulfur, in the form of hydrogen sulfide, was obtained in amount equal to 28% of the weight of initial sulfide. By analogy with β-tetralylnonylsulfide, the following course can be offered:



and secondary processes, proceeding according to Equations (1) and (2).

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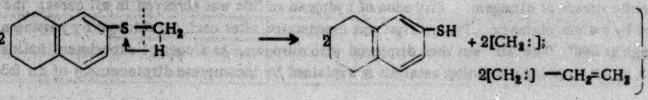
* Concerning conversion of aliphatic mercaptans into alkenes and hydrogen sulfide, see the earlier published work [1].

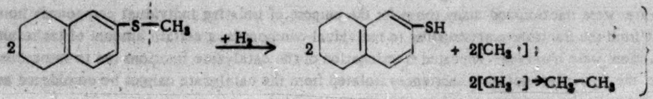
The presence of β-thiotetralol has indicated that bond ruputre occurs between sulfur and the cyclohexane ring. The cyclohexane formed changes further, according to Equation (8), converting completely into methylcyclopentane, which was isolated from the catalyzate. The possibility of conversion of cyclohexane into methylcyclopentane under conditions of contact with sulfur compounds was proved earlier by the authors [7]. The absence of cyclohexanethiol in the catalyzate does not indicate that bond rupture between sulfur and tetraline does not occur; the possibility exists that such a rupture has occurred, and that the cyclohexanethiol formed has converted into methylcyclopentane according to Equation (8)*; however, it could not be proved in the case given. Consequently, in the case of β-tetralylcyclohexylsulfide, bond rupture between the cyclohexane ring and sulfur was proved, and was accompanied by disproportionation of hydrogen.

Of special interest was conversion of β-tetralylmethylsulfide, where the simplest radical, methyl, was bound by one of the sulfur valences. As is known, a compound containing the methyl group differs in its composition from the higher homologs in certain characteristic properties. It was reasonable to expect the same peculiarity from β-tetralylmethylsulfide as well.

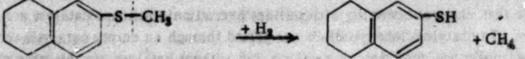
Upon contact with aluminosilicate, the following course for the processes could be assumed. In the case of bond rupture between sulfur and methyl groups



(9)



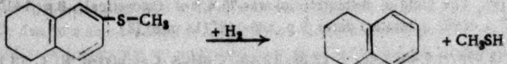
(10)



(11)

and processes proceeding according to Equations (1) and (2).

In the case of bond rupture between sulfur and the tetralin nucleus:



(12)

$$2CH_3SH \rightarrow CH_3{-}S{-}CH_3 + H_2S \qquad (13)$$

and the processes according to Equation (2).

Equation (9) reflects a characteristic for the reaction of aliphatic-aromatic sulfides, with bond rupture between sulfur and the alkyl and disproportionation of hydrogen. The specificity of the given case lies in the fact that the alkene which is formed, methylene, is unable to exist. Therefore, the ethylene present in the outgoing gases could be presumed to have been formed as the result of combination of the methylene with itself. The reaction course according to Equation (10) could lead to formation of ethane via the methyl radical stage. In the case of destructive hydrogenation (Equation 11), the methyl radical should convert to methane. Bond rupture between sulfur and alkyl according to any of these equations leads to formation of β-thiotetralol, which converts into tetralin and naphthalene, as the result of a secondary process (Equations 1 and 2). Rupture between sulfur and the tetralin radical (Equation 12) would give methyl mercaptan and tetralin, which, as a result of secondary processes (Equations 13 and 2) could convert into dimethyl sulfide and naphthalene.

As the result of contact of β-tetralylmethylsulfide with aluminosilicate, there were isolated from the catalyzate tetralin (35% of the catalyzate weight), naphthalene (36%), dimethylsulfide (15.6%), and β-thiotetralol (6%). Methyl mercaptan was trapped out of the exit gases, in the amount of 1.5% sulfur of the original weight of sulfide, and hydrogen sulfide (5.6% sulfur). Analysis of the gas freed from hydrogen sulfide and methyl mercaptan indicated that the hydrocarbons present contained only a trace of methane. There was no ethylene or ethane. The following conclusions could be drawn from these data: inasmuch as the outgoing gases did not contain ethane and ethylene, Equations (9) and (10) do not correspond to actuality. The presence of four possible primary reaction products — β-thiotetralol, methane, tetralin, and methyl mercaptan — in the liquid catalyzate and in the gases, indicated that the process proceeds simultaneously according to both Equation (11) and Equation (12). Hence, in the case of β-tetralylmethylsulfide, molecular rupture occurs at both of the sulfur bonds with radicals, similarly to that found above for β-tetralylnonylsulfide. The presence of naphthalene, dimethylsulfide, and hydrogen sulfide, which appeared to be secondary reaction products, indicated a further change of the primary reaction products according to Equations (1), (9), and (13)*. The course of the destructive hydrogenation reaction upon rupture of the bond between sulfur and alkyl (Equation 11) has been observed for the first time by the authors; in this fact the specificity of conversion of sulfides containing a methyl radical over aluminosilicate is inherent. The reaction proceeds according to Equation (11), since it cannot proceed by the usual scheme for aliphatic-aromatic sulfides.

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* Conversion of cyclohexanethiol into methylcyclopentane was described in an earlier published work [1].

EXPERIMENTAL

The synthesized sulfur compounds were passed over aluminosilicate under identical conditions. 23 g of catalyst was placed in a reaction tube, 1.5 cm in diameter. Length of the catalyst layer was 30 cm. The volumetric rate at which the substance was passed over catalyst was 0.25. In all experiments the reaction was carried out at 300° in a gentle stream of nitrogen. Evolution of hydrogen sulfide was observed in all cases; the hydrogen sulfide was trapped by sodium plumbite. The catalyst was regenerated after each experiment by passing a strong stream of air through at 500°. The air was then displaced with nitrogen. As a control experiment indicated, the presence of oxygen in the outgoing gas during catalysis is explained by incomplete displacement of air from the apparatus.

The catalyzates were fractionated many times for the purpose of isolating individual compounds from them. In each case, apart from the fractions corresponding to individual compounds, a certain amount of tar resulted. No lower cracking fractions were observed. Repeated fractionation of the catalyzate fractions led to some loss of substance. Therefore, the percentage ratios of substances isolated from the catalyzate cannot be considered as accurate, but only qualitatively characteristic of the catalyzate composition.

In order to prove that changes occurring with sulfides over aluminosilicate catalyst are not the result of thermal decomposition, β-tetralylcyclohexylsulfide was passed through an empty catalysis tube at 300° in a stream of nitrogen, i.e., under the conditions of catalysis, but without catalyst. In this case unchanged β-tetralylcyclohexylsulfide was obtained.

β-Thiotetralol resulted from reduction of β-tetralin sulfochloride [8], which was synthesized by interaction of tetralin with chlorosulfonic acid [9]. The yield of β-tetralinsulfochloride was 53% of theoretical. M.p. 54-56°. Literature data: m.p. 58° [9]. The yield of β-thiotetralol was 75.4% of theoretical. B.p. 141° (12 mm); 135° (8 mm); n_D^{20} 1.5972; d_4^{20} 1.0898. Literature data: b.p. 146-148° (14 mm) [8].

Found %: C 73.04, 73.09; H 7.45, 7.40; S 19.39, 19.40. $C_{10}H_{12}S$. Calculated %: C 73.12; H 7.36; S 19.52.

17.8 g of β-thiotetralol was passed over aluminosilicate catalyst. Weight of the resulting catalyzate was 11.8 g (66% of the thiol weight). The hydrogen sulfide evolved during catalysis was precipitated with sodium plumbite. Weight of the resulting PbS was 5.5 g, which corresponded to 0.74 g of sulfur (21.3% of the sulfur weight in initial thiol). A large amount of elementary sulfur was found in the catalyzate by shaking with metallic mercury. Tetralin, naphthalene, and the initial β-thiotetralol were isolated from the catalyzate. The weights and constants for the compounds isolated are given in Table 1.

After removal of hydrogen sulfide, the outgoing gas contained CO_2 0.2%; O_2 1.1%; saturated compounds, 0.3%; The remainder — nitrogen, in a stream of which the experiment was carried out.

TABLE 1

Catalysis of β-Thiotetralol

Substance isolated from catalyzate	Weight (in g)	Weight in % of catalyzate wt	Melting point (°C)	Boiling point	n_D^{20}	d_4^{20}
Tetralin **	4.0	33.9	–	77.5-78.5° (6 mm)	1.5445	0.9703
Naphthalene ***	3.3	27.9	80	–	–	–
β-Thiotetralol	0.8	6.8	–	122° (4 mm)	1.5990	1.0901

β-Tetralylnonylsulfide was synthesized for the first time by the general method of sulfide synthesis [10] from β-thiotetralate and nonyl bromide. The yield of β-tetralylnonylsulfide was

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* Conversion of aliphatic mercaptans into the corresponding sulfide is described in a work published earlier by the authors [1].

** Literature data: b.p. 90.8-91.2° (17 mm) [11]; n_D^{20} 1.5438 [12]; d_4^{20} 0.9707 [12].

*** Naphthalene picrate m.p. 150°. Literature data: naphthalene, b.p. 80.4° [13]; naphthalene picrate m.p. 149-149.5° [4].

41 g (68% of theoretical); b.p. 218.5-219.5° (4 mm); n_D^{20} 1.5370; d_4^{20} 0.9671.

Found %: C 78.70, 78.66; H 10.88, 10.82; S 10.46, 10.50. $C_{19}H_{30}S$. Calculated %: C 78.57; H 10.41; S 11.02.

30.0 g of β-tetralylnonylsulfide was passed over aluminosilicate catalyst. 20.9 g of liquid catalyzate was obtained (69.7% of the sulfide weight). The hydrogen sulfide evolved during catalysis gave 4.8 g of PbS, which corresponded to 0.64 g of sulfur (19.3% of the weight of sulfur in the original sulfide). From the catalyzate nonene-1, nonyl mercaptan, tetralin, naphthalene, and β-thiotetralol were separated. Nonyl mercaptan and tetralin, usually unseparable by ordinary fractionation because of the proximity of their boiling points, were separated from one another by precipitating the mercaptan with an alcoholic solution of sodium plumbite and then filtering the precipitate of $(C_9H_{19}S)_2Pb$. Tetralin was separated from the filtrate and from the lead nonyl mercaptide, by acidification with hydrochloric acid, the nonyl mercaptan was regenerated. The weights and constants of the compounds precipitated are given in Table 2.

TABLE 2

Catalysis of β-Tetralylnonylsulfide

Substances separated from the catalyzate	Weight (in g)	Weight (in % of catalyzate wt.)	Melting point	Boiling point	n_D^{20}	d_4^{20}
Tetralin *	5.5	26.8	–	97.5-100.5° (20 mm)	1.5442	0.9687
Nonene-1 **	3.3	15.7	–	146-150 (756 mm)	1.4120	0.7267
β-Thiotetralol ***	2.6	12.4	–	136 (8 mm)	1.5985	1.0890
Naphthalene ****	0.9	4.3	80°	–	–	–
Nonylmercaptan *****	0.8	3.8	–	101.5-102.5 (20 mm)	1.4555	0.8420

* Literature data: see annotations to Table 1.

** Literature data: b.p. 146° [15]; n_D^{20} 1.4169; d_4^{20} 0.7296 [16].

*** See above for β-thiotetralol.

**** Literature data: see annotations to Table 1. The naphthalene picrate had m.p. 150°.

***** Literature data: b.p. 91.9-92.4° (10 mm); n_D^{20} 1.4537; d_4^{20} 0.84015 [17].

Synthesis of β-tetralylcyclohexylsulfide. An attempt to synthesize β-tetralylcyclohexylsulfide, not described in the literature, from the potassium derivative of β-thiotetralol and cyclohexylbromide gave poor results: yield did not exceed 27%, due to a side reaction of cyclohexane formation from cyclohexylbromide under the influence of alkali. A series of experiments was set up for the purpose of increasing the sulfide yield, in which initial substances, temperature conditions, heating time were varied. β-Thiotetralol, alkali, and halide were taken in equimolecular quantities. The experimental results are given in Table 3.

TABLE 3

Synthesis of β-Tetralylcyclohexylsulfide

No.	Quantity of initial β-thiotetralol (g)	Alkali	Halide	Temperature of experiment	Heating time (in hours)	β-Tetralylcyclohexylsulfide Yield (% of theoretical)	n_D^{20}
1	20	KOH	$C_6H_{11}Br$	60-80°	1.5	25.0	1.5803
2	80	KOH	$C_6H_{11}Br$	75-86	2.0	27.0	1.5804
3	20	NaOH	$C_6H_{11}Br$	75-85	2.0	32.5	1.5797
4	53	NaOH	$C_6H_{11}Br$	68-75	2.0	30.3	1.5805
5	20	KOH	$C_6H_{11}Cl$	85-95	3.0	18.9	1.5802
6	10	KOH	$C_6H_{11}Cl$	118-123	6.0	31.6	1.5805
7	24	NaOH	$C_6H_{11}Cl$	115-124	10.0	34.9	1.5812

A maximum yield of β-tetralylcyclohexylsulfide (35%) was obtained by heating cyclohexylchloride with sodium thiotetralate for 10 hours at 115-123°. Cyclohexene formation in larger or smaller amounts was observed in all experiments. The resultant β-tetralylcyclohexylsulfide was redistilled in vacuo; b.p. 187.5-188.5° (3 mm); n_D^{20} 1.5800; d_4^{20} 1.0543.

Found %: C 78.28, 78.11; H 8.95, 8.96; S 13.03, 12.94. $C_{16}H_{22}S$. Calculated %: C 77.99; H 9.00. S 13.01.

40.4 g of β-tetralylcyclohexylsulfide was passed over aluminosilicate catalyst. 33.0 g of catalyzate was obtained (81.7% of the sulfide weight). Hydrogen sulfide from the outgoing gases gave 11.0 g of PbS, which corresponded to 1.47 g of sulfur (27.95% sulfur of the original sulfide weight). Upon fractionating the catalyzate, the following low boiling fractions were isolated: 1) b.p. 72-74°, n_D^{20} 1.4138; 2) b.p. 75-76°, n_D^{20} 1.4230. These fractions were apparently a mixture of three closely-boiling hydrocarbons: methylcyclopentane (b.p. 72.0-72.2°, n_D^{21} 1.4088 [18]), 1-methylcyclopentene-1 (b.p. 75-76°, n_D^{20} 1.4270 [19]), and 1-methylcyclopentene-2 (b.p. 69°, n_D^{18} 1.4222 [20]). The fractions did not contain sulfide. To determine the amount of unsaturated compounds, the iodine numbers of the fractions were determined. The iodine number for the first fraction was equal to 38.3; the percentage unsaturation was 12.52. The iodine number for the second fraction was equal to 68.3; the percentage unsaturation was 22.29. Hence both fractions contained a negligible amount of methylcyclopentene. Both fractions were combined and treated with an equal volume of 90% sulfuric acid. Upon distillation of the residue, methylcyclopentane resulted. Tetralin, naphthalene, β-thiotetralol, and the initial β-tetralylcyclohexylsulfide were separated by fractionation of the higher-boiling portions of the catalyzate. The weights and constants for the compounds obtained are given in Table 4.

TABLE 4

Catalysis of β-Tetralylcyclohexylsulfide

Substance isolated from catalyzate	Weight (in g)	Weight (in % of catalyzate weight)	Melting point	Boiling point	n_D^{20}	d_4^{20}
Tetralin *	9.2	27.88	–	74-75° (4 mm)	1.5465	0.9700
β-Thiotetralol *	6.1	18.48	–	135° (8 mm)	1.5985	1.0889
Methylcyclopentane **	5.51	16.69	–	72.5-73.5°	1.4119	0.7413
Naphthalene *	2.3	6.96	80°	–	–	–
β-Tetralylcyclohexylsulfide	1.0	3.03	–	–	1.5818	–

* Literature data – see annotation to Tables 1 and 2. Naphthalene picrate had m.p. 150°.

** Literature data: b.p. 72-72.2°; n_D^{21} 1.4088; d_4^{21} 0.7474 [18].

TABLE 5

Catalysis of β-Tetralylmethylsulfide

Substance isolated from the catalyzate	Weight (in g)	Weight (in % of catalyzate weight)	Melting point	Boiling point	n_D^{20}	d_4^{20}
Tetralin *	8.0	34.63	–	77.5° (8 mm)	1.5445	0.9712
Naphthalene *	8.4	36.36	80°	–	–	–
Dimethylsulfide **	3.6	15.58	–	33-39°	1.4418 (at 13.5°)	0.8534 (at 13.5°)
β-Thiotetralol *	1.3	5.63	–	136° (8 mm)	1.5990	1.0903

* Literature data: see annotation to Tables 1 and 2. Naphthalene picrate had a m.p. of 149.5°.

** Literature data: b.p. 37.2°; d_4^{20} 0.8449 [24].

β-Tetralylmethylsulfide was synthesized from potassium β-thiotetralate and methyl iodide [10]. The yield of β-tetralylmethylsulfide was 74.67 % of theoretical. B.p. 155° (12 mm); n_D^{20} 1.5920; d_4^{20} 1.0711. Literature data: b.p. 158-159° (10 mm) [21].

32 g of β-tetralylmethylsulfide was passed over aluminosilicate catalyst. The catalyzate weight was 31 g (74 % of the sulfite weight). The exit gases contained hydrogen sulfide and methyl mercaptan, separated by selective precipitation in the form of $(CH_3S)_2Pb$ and CdS [22]. The resulting mercaptide gave a positive reaction for CH_3SH with concentrated H_2SO_4 and with isatin a green coloration [23]. CdS was converted into PbS. 2.4 g of PbS was obtained, which corresponded to 0.34 g of H_2S, or 0.32 g of sulfur (5.56% sulfur of the original sulfide); and 6.7 g of $(CH_3S)_2Pb$, which corresponded to 1.07 g of CH_3SH or 0.71 g of sulfur (12.36% sulfur weight of original sulfide). Dimethylsulfide, tetralin, naphthalene, and β-thiotetralol were separated from the catalyzate. Tetralin and β-thiotetralol contained considerable elementary sulfur, which was removed with metallic mercury. The weights and constants of the substances synthesized are given in Table 5.

The dimethylsulfide gave a clear-cut positive reaction for sulfur sulfide with mercurous nitrate. The outgoing gas (1600 ml) from the catalysis contained 4.4% O_2 and 0.7% saturated compounds, after removal of the hydrogen sulfide. The remainder was nitrogen, in a stream of which catalysis was carried out. Upon calculating the n number for the formula of a saturated hydrocarbon C_nH_{2n+2}, it was found that n = 1. The gas contained only traces of methane, less than 1%. There was no ethane in the gas. The number, n, for the formula of saturated hydrocarbons was calculated in the following manner: from each milliliter of saturated hydrocarbon C_nH_{2n+2} there results on combustion n ml of CO_2. Hence, $n = \frac{\Delta CO_2}{\Delta V}$, where ΔCO_2 = the volume of carbon dioxide obtained on burning saturated hydrocarbons; ΔV = the volume of saturated gases taken for combustion.

The behavior of tetralin over aluminosilicate catalyst was studied for an explanation of the catalytic conversion mechanism.

30.0 g of tetralin (b.p. 81.5-82.5° (8 mm); n_D^{21} 1.5412; d_4^{20} 0.9671) was passed over aluminosilicate under catalytic conditions of the sulfur compounds. 29.2 g of catalyzate resulted (97.33% of the tetralin weight). The catalyzate was cooled with solid carbon dioxide, and the naphthalene which separated out on the funnel at −13° was filtered. At this temperature the tetralin melted and went into the filtrate, naphthalene remaining on the filter. 0.4 g of naphthalene was isolated with m.p. of 80°. The yield of naphthalene constituted 1.4% of the catalyzate weight. The exit gas contained 0.9% CO_2; unsaturated compounds: 0.3%; O_2 1%; CO 0.3%; H_2 0.1%; saturated (C_nH_{2n+2}) 2.9%. Saturated hydrocarbon − methane (n = 1). The remainder was nitrogen, in a stream of which the experiment was carried out. Thus, the gas contained about 3 volume percent of methane and traces of remaining gases.

19.9 g of tetralin was passed over aluminosilicate catalyst under catalytic sulfur conditions in a stream of nitrogen mixed with hydrogen sulfide. By double freezing of the catalyzate with solid carbon dioxide, with subsequent filtration at −13°, 0.9 g of naphthalene was isolated, which constituted 4.64% of the catalyzate weight. M.p. 80°. Thus, the presence of hydrogen sulfide facilitated dehydrogenation of the tetralin.

For clarification of the thermal stability of the β-tetralin series of sulfides, 19.6 g of β-tetralylcyclohexylsulfide (n_D^{20} 1.5792, d_4^{20} 1.0521) was passed through empty catalytic tubes in a stream of nitrogen at 300°. 19.0 of catalyzate resulted (96.94% of the sulfide weight) whose constants coincided with the constants of the sulfides investigated (n_D^{20} 1.5794, d_4^{20} 1.0527).

SUMMARY

1. β-Thiotetralol, upon contact with aluminosilicate at 300°, converts into tetralin, naphthalene, and hydrogen sulfide. Naphthalene forms by dehydrogenation of tetralin. The phenomenon of dehydrogenation of the hexamethylene ring to the benzene ring under the conditions of contact with sulfur compounds has been observed for the first time.

2. Upon contact of β-tetralylnonylsulfide and β-tetralylmethylsulfide with aluminosilicate, there occurs rupture of the molecule at both valences which bind sulfur to the radicals. With aliphatic-aromatic sulfides under identical conditions, the bond between sulfur and alkyl, only, is ruptured. Weakening of the bond between the benzene ring and the sulfur in β-tetralino-aliphatic sulfides can be explained by the effect of the hexamethylene ring which is condensed with benzene in the tetralin molecule.

3. Alkenes form from aliphato-tetralin and aliphato-aromatic sulfides upon their contact with aluminosilicate as a result of hydrogen disproportionation. β-Tetralylmethylsulfide represents an exception: upon rupture of the bond between methyl and sulfur, there has been observed for the first time destructive dehydrogenation with sulfides of this type, which is related to the impossibility of existenceof methylene.

4. Rupture of the bond between sulfur and the hexamethylene nucleus has been proved for β-tetralylcyclohexylsulfide, analogous to the behavior of naphthene-aromatic sulfides.

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RESEARCH IN THE FIELD OF AMINO ACIDS

V. THE CONDENSATION REACTION OF ALDEHYDES AND KETONES WITH ACYLGLYCINES

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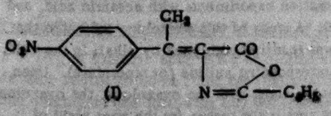
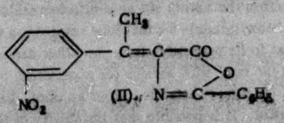
Numerous investigations on the condensation reaction of aldehydes with acylglycines (the Erlenmeyer reaction) have indicated that the character of the aldehyde radical affects the course of this reaction. Aromatic aldehydes and a majority of the heterocyclic aldehydes enter readily into reaction with hippuric acid to form oxazolones in good yields [1]. Aldehydes of the aliphatic series react with difficulty with hippuric acid [2], and under analogous conditions, do not react with aceturic acid. Of the aliphatic-aromatic aldehydes, phenylacetaldehyde and phenylpropionic aldehyde do not react with hippuric acid [3]. The nature of the substituents in the ring of aromatic aldehydes apparently does not affect the direction of the reaction (as distinguished from the Perkin reaction). There are characteristic indications for the fact that the presence of a nitro group in the ortho position to the aldehyde group in some cases lowers, and in others increases, the yield of oxazolone. Thus, upon condensing 2-nitro-3,4-methylenedihydroxybenzaldehyde with hippuric acid, the yield of oxazolone was 35-42% [4], while condensation of 3,4-methylenedihydroxybenzaldehyde with hippuric acid resulted in a 67% yield of the oxazolone [5], or 82% [6]; oxazolone resulted in 84% yield [7] from 2-nitro-5-methoxybenzaldehyde, while the yields of corresponding oxazolones from the methoxybenzaldehydes did not exceed 80%.

Evidently, in the cases indicated, reaction conditions for the condensation have an effect, but not the presence of the nitro-group. The condensation reaction of o-nitrobenzaldehyde with hippuric acid can serve as an example to confirm the effect of reaction conditions upon the yield of oxazolone. According to the literature data, 2-phenyl-4-(2-nitrobenzylidene)-5-oxazolone results in 60% yield [8], or 61.2% [7]. But when this reaction was carried out by the authors under other conditions, i.e., using potash in place of sodium acetate (see Experimental), the same oxazolone then resulted in 80-85% yield.

A study of the condensation reaction of ketones with hippuric acid has indicated a somewhat different relation between the ketone radical structure and its ability to enter into a condensation reaction with hippuric acid. Acetone [9], methylethylketone [10], cyclohexanone [11], and benzylideneacetone [12] react with hippuric acid to form the oxazolones in yields of 73, 67, 49, and 46%, respectively. It is apparently impossible to increase the yields, due to the existence of a supra-acylation process which occurs simultaneously with the condensation process. Upon condensing acetone and methylethylketone with hippuric acid, sodium benzoate was obtained in the amount of 20-30% of the hippuric acid taken.

Attempts were made to obtain the oxazolone of acetophenone [11], but it was found that acetophenone does not react with hippuric acid. The author also studied the possibility of condensing acetophenone with hippuric acid under various conditions; during this time several compounds were synthesized, among them 2-phenyl-4-(1'-hydroxyethylidene)-5-oxazolone, but the oxazolone sought for was not found. It appeared of interest to the authors to verify the effect of the nitro group in the molecule of aliphatic-aromatic ketone upon the ability of the carbonyl group to enter into reaction with hippuric acid. For this purpose, experiments were set up for condensing p- and m-nitroacetophenone with hippuric acid. In both cases, the corresponding oxazolones resulted — (I) and (II).


(I)


(II)

wherein 2-phenyl-4-[1'-(p-nitrophenyl)ethylidene]-5-oxazolone (I) was isolated in two crystalline modifications — red and yellow. The yellow-colored crystals were the stable form; the red-colored crystals dissolved in organic solvents to precipitate as the yellow crystals.

As indicated above, aldehydes of the aliphatic series entered, with difficulty, into condensation reaction with hippuric acid, and polymerization products resulted along with the oxazolone. Various investigators have changed the Erlenmeyer reaction conditions for the purpose of eliminating the polymerization reaction and of increasing the yield of oxazolone. One of them [13] used lead acetate in place of sodium acetate, while others did not introduce all of the aldehyde at once into the reaction medium, but instead added it gradually, dropwise, eliminating in this way prolonged contact of aldehyde with the reaction medium. Both modifications give positive results.

On the basis of accumulated research material on the Erlenmeyer reaction, investigators have come to the conclusion that reaction proceeds through the formation of 2-phenyl-5-oxazolone, and not through formation of the unsaturated acylated amino acid. When hippuric acid undergoes cyclization into 2-phenyl-5-oxazolone, there is formed acetic acid, which changes the pH of the medium, which perhaps facilitates polymerization of aldehydes in the aliphatic series. Sodium acetate does not seem to be a sufficiently good buffer under the conditions of acetic acid formation, and when substituted by lead acetate, or when the effect of acetic acid on the aldehyde was removed by a gradual introduction of the latter into the reaction medium, there was then obtained from acetaldehyde 2-phenyl-4-ethylidene-5-oxazolone in 47-60% yield, and from isobutyraldehyde 2-phenyl-4-isobutylidene-5-oxazolone in 31% yield [13] instead of 8%.

The method proposed in 1950 [6] for synthesizing oxazolones by using potash in place of sodium acetate increased by 10-15% the yields of oxazolones from aromatic aldehydes. Apparently, in the case of aromatic aldehyde condensations with acylglycines, acetic acid affects this process unfavorably. However, in the presence of potash, the acetic acid is neutralized, and the yields of oxazolones are therefore greater than when sodium acetate is used. The reaction of aromatic aldehydes with hippuric acid in the presence of potash begins at room temperature, and is then accompanied by evolution of heat, whereupon the temperature changes sharply, depending upon the character of the aldehyde. Aromatic aldehydes react with aceturic acid upon heating, but the oxazolones are not always obtained in good yields. Benzaldehyde reacts with hippuric and with aceturic acids with good yields (Table 1). However, substituted benzaldehydes, with aceturic acid, do not always produce oxazolones in good yields. From p-methoxybenzaldehyde and aceturic acid, oxazolone results in maximum yield of 50%. It was of interest to the author to clarify the influence of a nitro group in the aldehyde molecule upon its condensation with aceturic acid. As indicated above, o-nitrobenzaldehyde reacted with hippuric acid to give the oxazolone in 80-85% yield. The reaction of o-nitrobenzaldehyde with aceturic acid has not been described in the literature.

TABLE 1

Oxazolone	Formula	Yield of oxazolone (in %) in the presence of:		
		CH_3COONa	K_2CO_3	$NaHCO_3$
2-Phenyl-4-benzylidene-5-oxazolone	$C_{16}H_{11}O_2N$	66	83.7	83.5
2-Methyl-4 benzylidene-5-oxazolone	$C_{11}H_9O_2N$	77	85	72.7-78
2-Phenyl-4 (p-methoxybenzylidene)-5-oxazolone	$C_{17}H_{13}O_3N$	80	80-85	85
2-Methyl-4 (p-methoxybenzylidene) 5-oxazolone	$C_{12}H_{11}O_3N$	35-45	40-50	25-30
2-Phenyl-4-(o-nitrobenzylidene)-5-oxazolone	$C_{16}H_{10}O_4N_2$	60	85	82
2-Methyl-4-(o-nitrobenzylidene)-5-oxazolone	$C_{11}H_8O_4N_2$	–	–	20
2-Phenyl-4-isopropylidene-5-oxazolone	$C_{12}H_{11}O_2N$	62.7	–	50-56
2-Phenyl-4-isobutylidene-5-oxazolone	$C_{13}H_{13}O_2N$	8	21	26
2-Phenyl-4-(1' phenylethylidene)-5-oxazolone	$C_{17}H_{13}O_2N$	0	0	0
2-Phenyl-4 [1' (p nitrophenyl)-ethylidene]-5-oxazolone	$C_{17}H_{12}O_4N_2$	–	28	31
2-Phenyl-4 [1' (m-nitrophenyl)-ethylidene]-5-oxazolone	$C_{17}H_{12}O_4N_2$	–	13-15	–

In this connection the author set up o-nitrobenzaldehyde condensation experiments with aceturic acid, and 2-methyl-4-(o-nitrobenzylidene)-5-oxazolone resulted in 20 25% yield. A study of this oxazolone indicated that it differed somewhat in its properties from the other oxazolones. It was readily hydrolyzed by alkali in the cold, and also reacted in the cold with aniline (or piperidine) to give the corresponding anilide (or piperidide). Upon recrystallization of technical oxazolone from alcohol, there was isolated, along with the oxazolone, the oxazolone acid and its ethyl ester. It is possible that instability of the oxazolone ring is the reason for the poor yield of oxazolone.

The author studied the condensation reaction of aldehydes and ketones with acylglycines in the presence of sodium bicarbonate, obtaining almost the same yields as when potash was used. In Table 1 the oxazolone yields, using potash and sodium bicarbonate, are given. With potash the reaction proceeded at room temperature, and with sodium bicarbonate, at 40-50°.

In the study of Erlenmeyer's reaction, the author noted the ability of saturated and unsaturated acylated amino acids to yield readily crystallizable salts with bases. The author obtained several quaternary ammonium salts of acylamino acids with piperidine (Table 2).

TABLE 2

Acylamino acid	Formula of the quaternary ammonium salt	Melting point	% N	
			Found	Calculated
Acetylleucine	$C_{13}H_{26}O_3N_2$	146-147°	10.84	10.51
Acetylvaline	$C_{12}H_{24}O_3N_2$	108-111	11.05	11.15
α-Benzoylaminocinnamic acid	$C_{21}H_{24}O_3N_2$	153-154	7.95	8.26
α-Acetylaminocinnamic acid	$C_{16}H_{22}O_3N_2$	152-153	9.65	9.24
α-Benzoylamino-β-isopropylacrylic acid	$C_{18}H_{26}O_3N_2$	109-116	7.90	7.86
α-Acetylamino-p-methoxycinnamic acid	$C_{17}H_{24}O_4N_2$	181-182	8.71	8.55
α-Benzoylamino-p-methoxycinnamic acid	$C_{22}H_{26}O_4N_2$	105-109	6.69	6.92

EXPERIMENTAL

I. 2-Phenyl-4-benzylidene-5-oxazolone

40 ml of acetic anhydride was added to a mixture consisting of 26.5 g of freshly-distilled benzaldehyde, 22.5 g of hippuric acid, and 17.25 g of anhydrous potash. After 3-5 minutes, evolution of carbon dioxide began, rapid dissolution of the initial products took place, and the whole solution immediately solidified, the temperature of the reaction mass rising to 120°. On the following day, the crystalline mass was ground with water, filtered, and washed, first with 10% acetic acid, and then with water, to the appearance of a transparent wash water. Air-dried. M.p. 165.5-167° A sample mixed with 2-phenyl-4-benzylidene-5-oxazolone melted without depression. The yield was 26.2 g, i.e., 83.79% of theoretical.

II. 2-Methyl-4-benzylidene-5-oxazolone.

14.75 g of aceturic acid, 8.6 g of anhydrous potash, 6.5 g of freshly distilled benzaldehyde, and 40 ml of acetic anhydride were mixed. Temperature of the reaction mass rose spontaneously to 30-32°, and evolution of carbon dioxide began. After 15 minutes, when the temperature began to decrease, the flask was gradually heated (to 60° after 25-30 minutes) and this temperature was maintained for 1 hour; violent evolution of carbon dioxide occurred during this time, with foaming of the entire mass and the separation of a crystalline precipitate. The foaming gradually subsided; the temperature was increased to 120° over a period of 1 hour, and then heated at 120-135° for another hour, whereupon the crystalline precipitate disappeared at 80° and the entire mass converted to a dark liquid which crystallized upon cooling. The crystals on the following day were ground with 75 ml of water and filtered The precipitate was washed with 10% acetic acid, water, and air-dried. The yield was 20.2 g (85% of the theoretical). M.p. 146-148°.

III. 2-Phenyl-4-(p-methoxybenzylidene)-5-oxazolone

2-Phenyl 4-(p-methoxybenzylidene)-5 oxazolone was synthesized under the same conditions as with 2-phenyl-4-benzylidene-5-oxazolone, the temperature not exceeding 46° when using potash, and the reaction being carried out at 60° when using sodium bicarbonate. The yield of 2-phenyl-4-(p-methoxybenzylidene)-5 oxazolone was 80-85%, m.p. 150 153°.

IV. 2-Phenyl-4-(o-nitrobenzylidene)-5-oxazolone

10 g of hippuric acid, 8.5 g of o-nitrobenzaldehyde, 4.7 g of sodium bicarbonate, and 20 ml of acetic anhydride were heated to 50-55°, and the temperature maintained to cessation of carbon dioxide evolution. Allowed to stand overnight; the following day the reaction mass was mixed with alcohol and filtered. The precipitate was washed with 2% soda solution, dried, and crystallized from acetic acid or alcohol. The yield was 82% M.p. 160-164°.

V. 2-Methyl-4-(o-nitrobenzylidene)-5-oxazolone.

5 g of aceturic acid, 6.5 g of o-nitrobenzaldehyde, 3.72 g of sodium bicarbonate, and 9.5 ml of acetic anhydride were heated on a water bath at 55-67° for 2 hours. Allowed to stand overnight. On the following day it was mixed with 10 ml of alcohol and filtered after 1 to 2 hours standing. The residue was crystallized from alcohol. After cooling the alcoholic solution a mixture of oxazolone and the ester of α-acetylamino-o-nitrocinnamic acid, m.p. 92-98°, precipitated. α-Acetylamino-o-nitrocinnamic acid remained in the alcoholic mother liquor. The mixture with a m.p. of 92-98° was mixed with a small quantity of ether. The undissolved portion was filtered off, and the ether distilled off. The residue represented 2-methyl-4-(o-nitrobenzylidene)-5-oxazolone and was crystallized from benzene. M.p. 110-112°.

Found %: N 12.03. $C_{11}H_8O_4N_2$. Calculated %: N 12.07.

The crystals of α-acetylamino-o-nitrocinnamic acid ethyl ester, which did not dissolve in the ether, were crystallized from benzene. M.p. 121-123°.

Found %: N 9.80. $C_{13}H_{14}O_5N_2$. Calculated %: N 10.03.

α-Acetylamino-o-nitrocinnamic acid. 0.5 g of 2-methyl-4 (o-nitrobenzylidene)-5-oxazolone and 5 ml of a 2% solution of sodium hydroxide were left standing for several hours to the complete dissolution of oxazolone. 15% hydrochloric acid was added to the transparent liquid, to an acid reaction with Congo red. It was filtered, washed with water, and dried. M.p. 201-203°, with decomposition. 0.52 g of α-acetylamino-o-nitrocinnamic acid resulted. The yield was 98%:

Found %: N 10.97; M 254.5. $C_{11}H_{10}O_5N_2$. Calculated %: N 11.19; M 250.08.

The anilide and piperidide of α-acetylamino-o-nitrocinnamic acid. 0.5 g of 2 methyl-4-(o-nitrobenzylidene)-5-oxazolone was dissolved in 10 ml of dry benzene, and 0.3 ml of aniline added to the solution. After several minutes the anilide began to precipitate, and was filtered off after 1-1.5 hours and washed with benzene and ether. It was crystallized from aqueous alcohol. The melting point of α-acetylamino-o-nitrocinnamic acid anilide was 199-201° (with decomposition):

Found %: N 12.58. $C_{17}H_{15}O_4N_3$. Calculated %: N 12 91.

0.5 g of methyl-4-(o-nitrobenzylidene)-5-oxazolone was dissolved in 10 ml of dry benzene, and 0.2 ml of piperidine was added to the solution. The solution became red in color and heat was spontaneously evolved. Benzene was distilled off in vacuo. The residue was ground with ether and filtered. It was recrystallized twice from 50% methyl alcohol. M.p. was 214-216°.

Found %: N 12.96 $C_{16}H_{19}O_4N_3$. Calculated %: N 13.24.

VI. 2-Phenyl-4-isopropylidene-5-oxazolone

10 g of hippuric acid, 4.6 g of sodium bicarbonate, 16 ml of acetic anhydride, and 165 ml of acetone were heated on a water bath at 60-63° for 6 hours. On the following day, the precipitate of sodium benzoate was filtered off; it was obtained in the amount of 23-29% (calculating on the basis of hippuric acid). The filtrate was evaporated in vacuo, and after 100-110 ml of acetone had distilled, the residue, while still warm, was poured into water and allowed to stand overnight. The precipitate was then filtered off, washed with water, 2% solution of soda, again with water, and then dried in the air. 6.6 g resulted, which was recrystallized from 80% alcohol. The yield was 5.6 g, i.e., 50% of the theoretical. The melting point of the 1-phenyl-4-isopropylidene-5-oxazolone was 94-97°. Upon condensing hippuric acid with methylethyl ketone under the conditions of Experiment VI, sodium benzoate was formed in the amount of 20-25%. 2-Phenyl-4-secondary-butylidene-5-oxazolone resulted as a mixture of two geometrical isomers.

VII. 2-Phenyl-4-[1'-(p-nitrophenyl)-ethylidene]-5-oxazolone.

3.26 g of hippuric acid and 1.26 g of anhydrous potash were mixed, and to the mixture was added 5.78 g of acetic anhydride Reaction started after 2-5 minutes, as evidenced by evolution of carbon dioxide bubbles. When carbon dioxide evolution decreased, 3 g of p-nitroacetophenone was introduced, and the temperature decreased 4-5° at the same time. The reaction mass was heated for 20 minutes at 44°. Gradual dissolution of the precipitate took place, and the entire mass then suddenly crystallized. It was heated up to 49° for some time and then left to stand overnight. On the following day a mixture of ice and water (40 g) was introduced into the flask, and after one hour standing, was filtered. The orange-colored precipitate was washed with water, 4% sodium bicarbonate, again with water, and dried. It was crystallized from alcohol. Oxazolone in the form of yellow crystals with m.p. 175-177° resulted. The yield was 28% of theoretical.

Found %: C 65.92; H 3.84; N 9.12. $C_{17}H_{12}O_4N_2$. Calculated %: C 66.21; H 3.92. N 9.09.

After the technical oxazolone was washed several times with alcohol to separate traces of initial product and the yellow oxazolone crystals, the red crystals of oxazolone were left behind. The melting point of these crystals was the same as for the yellow crystals. The red oxazolone dissolved with heating in alcohol, benzene, and dioxane. It precipitated from the solutions as the yellow crystalline form. The red crystals dissolved in pyridine in the cold, and were precipitated by water from solution as the yellow crystals.

α-Benzoylamino-β-(p-nitrophenyl)-crotonic acid. 0.5 g of 2-phenyl-4-[1-(p-nitrophenyl)-ethylidene]-5-oxazolone was boiled for 5 minutes with 10 ml of a 2% solution of sodium hydroxide. Carbon was added to the turbid solution, filtered, and the solution acidified with hydrochloric acid to Congo red. The colorless crystals were filtered off. The yield was 0.43 g (81% of theoretical). Upon recrystallization from alcohol, the α-benzoylamino-β-(p-nitrophenyl)-crotonic acid melted at 202-204° (with decomposition).

Found %: N 8.58. $C_{17}H_{14}O_5N_2$. Calculated %: N 8.61.

The methyl ester of α-benzoylamino-β-(p-nitrophenyl)-crotonic acid. 0.25 g of oxazolone was dissolved in 25 ml of methyl alcohol, to which traces of sodium alcoholate were added, and left to stand for 24 hours. It was then dissolved in water and the resulting precipitate filtered off. It was crystallized from 80% alcohol. The melting point of the methyl ester of α-benzoylamino-β-(p-nitrophenyl)-crotonic acid was 181-183°.

The anilide of α-benzoylamino-β-(p-nitrophenyl)-crotonic acid. 0.5 g of 2-phenyl-4-[1-(p-nitrophenyl)-ethylidene)-5-oxazolone, 0.2 g of aniline, and 10 ml of dry benzene were boiled for 2 hours. After cooling, it was filtered off; the mother liquor was evaporated in vacuo, the resulting precipitate added to the first and ground with a small quantity of ether. 0.52 g resulted, i.e., 81% of theoretical. The anilide of α-benzoylamino-β-(p-nitrophenyl)-crotonic acid, recrystallized from benzene-acetone mixture (2:1), melted at 251-252° (decomposition).

Found %: C 68.89; H 4.65. $C_{23}H_{19}O_4N_3$. Calculated %: C 68.80; H 4.77.

The piperidide of α-benzoylamino-β-(p-nitrophenyl)-crotonic acid. Upon heating 2-phenyl-4-[1-(p-nitrophenyl)-ethylidene]-5-oxazolone with piperidine, the piperidide of α-benzoylamino-β-(p-nitrophenyl)-crotonic acid resulted, and, after crystallization from dioxane, melted at 211-213° (with decomposition).

Found %: N 10.89. $C_{22}H_{23}O_4N_3$. Calculated %: N 10.67.

VIII. 2-Phenyl-[1'-(m-nitrophenyl)-ethylidene]-5-oxazolone.

1.9 ml acetic anhydride was added to a mixture of 1.09 g of hippuric acid and 0.42 g of potash. 1 g of m-nitroacetophenone was then introduced and the temperature gradually brought up to 60° within an hour. It was allowed to stand overnight at room temperature. It was treated as in the preceding experiment. 2-Phenyl-4-[1'(m-nitrophenyl)-ethylidene]-5-oxazolone was recrystallized from ethyl acetate. M.p. 174-176°. The yield was 0.25 g, i.e., 13.3 % of the theoretical.

Found %: N 9.18. $C_{17}H_{12}O_4N_2$. Calculated %: N 9.09.

Upon heating the oxazolone with a 2% solution of sodium hydroxide, α-benzoylamino-β-(m-nitrophenyl)-crotonic acid resulted. It was crystallized from alcohol. M.p. 197-198°, with decomposition.

Found %: N 8.33. $C_{17}H_{14}O_5N_2$. Calculated %: N 8.58.

The piperidide of α-benzoylamino-β-(m-nitrophenyl)-crotonic acid. 0.25 g of 2-phenyl-4-[1'-(m-nitrophenyl)-ethylidene]-5-oxazolone, 0.59 g of piperidine, and 8 ml of dry benzene were boiled for 1 hour. The resulting solution was evaporated in vacuo. The residue was ground with ether and crystallized from alcohol-dioxane mixture (3:1). The melting point of the piperidide of α-benzoylamino-β-(m-nitrophenyl-crotonic acid was 216-217° (with decomposition).

Found %: N 10.87. $C_{22}H_{23}O_4N_3$. Calculated %: N 10.67.

IX. Quaternary ammonium compounds of saturated and unsaturated amino acids with piperidine.

All of the salts indicated in Table 2 were obtained in the same manner as that described below for the salt of acetylleucine with piperidine. 0.5 g of acetylleucine was mixed with 10 ml of dry benzene, and 0.5 ml of piperidine was added to the resulting suspension. After addition of the piperidine, the precipitate was dissolved, and then a crystalline precipitate began to separate from the solution. The yield was 0.6 g. It was crystallized from a mixture of methyl alcohol and acetone, or was dissolved in methyl alcohol and precipitated with acetone. M.p. 146-147°.

Found %: N 10.51. $C_{13}H_{26}O_3N_2$. Calculated %: N 10.84.

SUMMARY

1. Acetophenone does not react with hippuric acid under conditions of the Erlenmeyer reaction. The nitro group, when introduced into the acetophenone molecule, activates the carbonyl group, and so nitroacetophenone reacts with hippuric acid.

2. 2-Methyl-4-o-nitrobenzylidene-5-oxazolone has been synthesized. It has been demonstrated that the properties of the oxazolone ring differ from those of the oxazolone ring of an unsaturated oxazolone, because this ring is readily split in the cold by alkalies and bases.

3. It has been demonstrated that the use of sodium bicarbonate in the condensation reaction of aldehydes and ketones with acylglycines makes it possible to synthesize oxazolones in the same yields as with potash.

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* See Consultants Bureau Translation, p. 1923.

CYCLOALKYLATION OF AROMATIC COMPOUNDS

VI. CONDENSATION OF 1-METHYLCYCLOPENTANOL AND 1-CHLORO-1-METHYLCYCLOPENTANE WITH BENZENE

N. G. Sidorova and E. A. Dubnikova

The alkylation of aromatic compounds by methylcyclopentane has received but little study. Condensation of 1-chloro-1-methylcyclopentane with benzene, phenol, and cresol in the presence of ferric chloride [1] has been described, as well as condensation of 1-methylcyclopentanol with phenol in the presence of aluminum chloride [2]. Upon condensing 1-chloro-1-methylcyclopentane with benzene, there were obtained a liquid monoalkylated product, 1-methyl-1-phenylcyclopentane in 37% yield (of theoretical), and a solid disubstituted product. The products were characterized only by their constants. However, there has been observed [3] production of 1-methyl-1-phenylcyclopentane as a result of the abnormal reaction of the acid chloride of 1-methylcyclopentane-1-carboxylic acid with benzene in the presence of aluminum chloride.

The authors studied condensation of 1-methylcyclopentanol with benzene in the presence of aluminum chloride. To avoid a possible isomerization, with expansion of the ring, we carried out the condensation under very mild conditions — in a large excess of benzene (15 moles) and with a very slow addition of aluminum chloride at room temperature. After standing for 24 hours, the reaction mixture was gradually brought to boiling. The monoalkylated hydrocarbon resulted in 43% yield; no definite product separated from the high-boiling fraction. To identify the monoalkylated product by the usual procedure, the nitro compound was obtained, m.p. 58°, which corresponded closely to the melting point for p-nitrocyclohexylbenzene. However, further conversion of the nitro-compound into the acetamino derivative gave a substance melting at 141°, as contrasted with a melting point of 130-131° for the acetaminocyclohexylbenzene. This result indicated definitely that the substance obtained by alkylation was 1-methyl-1-phenylcyclopentane. It was characterized by a large number of derivatives.

For an explanation of the existence of cyclic isomerization in this reaction, the condensation was carried out under harsher conditions — with a small benzene excess and rapid $AlCl_3$ addition, which was accompanied by a boiling up of the reaction mixture. The hydrocarbon resulting from this operation was also found to be mainly the 1-methyl-1-phenylcyclopentane.

An attempt to effect condensation in the presence of phosphoric acid led to a substance of strong aroma, resembling mint, apparently the methylcyclopentane dimer (possibly with an impurity of alkylation product).

In addition, condensation of 1-chloro-1-methylcyclopentane with benzene was carried out by the authors; two hydrocarbons were obtained — 1-methyl-1-phenylcyclopentane (33%) and p-di-(1-methylcyclopentyl)-benzene with m.p. 92°.

The results indicated that under the conditions of these condensations there is no significant isomerization of five-membered rings to six-membered, whereas individual homologs of cyclopentane, according to the data of Turova-Polyak [4], convert to a considerable degree into cyclohexane under the action of aluminum chloride.

EXPERIMENTAL

1-Methylcyclopentanol was obtained from CH_3MgI and cyclopentanone [5]. The yield was 45% of theoretical. B.p. 75° (80 mm); m.p. 35-37°.

1-Chloro-1-methylcyclopentane was obtained by the action of fuming hydrochloric acid upon 1-methylcyclopentanol. After a half-hour shaking with pre-cooled reagents, the mixture was left to stand, the upper layer washed with sodium bicarbonate solution, then with water, dried with calcium chloride, and finally distilled. The yield was 55% of theoretical. B.p. 66-67° (160 mm); n_D^{20} 1.4455.

Condensation of 1-Methylcyclopentanol with Benzene

Condensation I. The reaction was carried out in the usual apparatus without stirrer. 6.5 g (0.05 mole) of aluminum chloride was added in small portions over a period of 2 hours with periodic vigorous shaking to 8 g (0.08 mole) of 1-methylcyclopentanol and 100 ml (1.1 mole) of benzene. Each portion was added only after complete dissolution of the preceding portion; no HCl evolution was observed in this procedure. After completion of the $AlCl_3$ addition, the mixture was allowed to stand overnight, and was then gradually heated to boiling on a boiling water bath. After cessation of HCl evolution the mixture was cooled and decomposed. After the usual treatment, 5.5 g (43%) was obtained of 1-methyl-1-phenylcyclopentane – a mobile liquid of pleasant odor, resembling that of carrots. B.p. 110-112° (25 mm); d_4^{20} 0.9396; n_D^{20} 1.5193; MR_D 51.69; calculated 51.82.

Found %: C 89.80; H 9.89. $C_{12}H_{16}$. Calculated %: C 90.00; H 10.00.

According to the literature data [1]: 1-methyl-1-phenylcyclopentane has a b.p. of 94-95° (10 mm); d_4^{20} 0.9446; n_D^{20} 1.5241.

p-Nitro-(1-methylcyclopentyl)-benzene. Obtained by treating 3 g of the hydrocarbon with 12 ml of nitrating mixture, at first in the cold, and then with heating on a warm water bath (50-60°). Separation was as usual. The yield was 2.55 g (66%). The b.p. was 130-133° (15 mm). Immediately following distillation, the nitro compound crystallized. The crystals were in the form of yellow needles with m.p. 55°. After three recrystallizations from alcohol, the melting point reached 58°.

5.13 mg substance: 0.350 ml N_2 (27°, 726 mm). Found %: N 7.06. $C_{12}H_{15}NO_2$. Calculated %: N 6.83.

The amine resulted on reduction with tin and hydrochloric acid, and after purification was converted to solid derivatives.

p-Acetamino-(1-methylcyclopentyl)-benzene. M.p. 140-141°. Platelets (from dilute alcohol).

4.31 mg substance: 0.280 ml N_2 (27°, 726 mm). Found %: N 6.73. $C_{14}H_{19}NO$. Calculated %: N 6.45.

p-Benzamino-(1-methylcyclopentyl)-benzene. M.p. 176° (from dilute alcohol). Fine, opaque needles in star clusters.

5.37 mg substance: 0.270 ml N_2 (19°, 731 mm). Found %: N 5.45. $C_{19}H_{21}NO$. Calculated %: N 5.02.

Picrate of p-(1-methylcyclopentyl)-aniline, melted with decomposition at 191-195°. Dark yellow, very fine needles (from benzene and ligroin mixture).

3.91 mg substance: 0.505 ml N_2 (20°, 739 mm). Found %: N 14.13. $C_{18}H_{20}N_4O_7$. Calculated %: N 13.86.

p-(1-Methylcyclopentyl)-benzenesulfonamide [6]. Thick, transparent needles (benzene + ligroin) with m.p. 137-138°.

10.72 mg substance: 0.603 ml N_2 (18.5°, 725 mm). Found %: N 6.05. $C_{12}H_{17}NSO_2$. Calculated %: N 5.86.

p-(1-Methylcyclopentyl)-benzenesulfoanilide. M.p. 118-119° Transparent prisms (from ligroin).

9.96 mg substance: 0.443 ml N_2 (18°, 729 mm). Found %: N 4.83. $C_{18}H_{21}NSO_2$. Calculated %: N 4.44.

Condensation II. 4.2 g (0.042 mole) of 1-methylcyclopentanol was taken for reaction, plus 15 ml (0.17 mole) of benzene and 3.4 g (0.026 mole) of $AlCl_3$. Addition of the $AlCl_3$ was carried out rapidly and caused violent evolution of HCl. Immediately following addition of all the $AlCl_3$, the mixture was boiled for 1 hour. Further treatment was as usual. 1.4 g (21%) of the alkylation product was obtained, consisting mainly of 1-methyl-1-phenylcyclopentane.

B.p. 104-107° (20 mm); n_D^{20} 1.5153; d_4^{20} 0.9296; MR_D 51.97. Calculated 51.82.

The acetamino derivative melted at 140°. The sample mixed with a sample of the amino derivative of 1-methyl-1-phenylcyclopentane obtained from the preceding reaction did not produce depression in melting point.

Condensation of 1-Chloro-1-methylcyclopentane with Benzene

The reaction was carried out in a two-necked flask with mechanical stirring. 0.5 g (0.004 mole) of aluminum chloride was added in several portions to a mixture of 8 g (0.07 mole) of the chloride and 100 ml (1.1 mole) of benzene cooled to −15°. The reaction mixture was heated on a water bath for 1 hour. After the usual treatment, 3.3 g (33%) of 1-methyl-1-phenylcyclopentane with b.p. 148-150° (100 mm) resulted, along with

0.8 g (10%) of p-di-(1-methylcyclopentyl)-benzene, which distilled at 150-200° (100 mm). M.p. 92° (from dilute alcohol).

According to the literature data: p-di-(1-methylcyclopentyl)-benzene melts at 94° [1].

The constants for 1-methyl-1-phenylcyclopentane were: b.p. 120-122° (30 mm); n_D^{20} 1.5194; d_4^{20} 0.9383; MR_D 51.83; calculated 51.82.

Found %: C 89.76; H 9.90. $C_{12}H_{16}$. Calculated %: C 90.00; H 10.00.

The nitrocompound: m.p. 58°.

SUMMARY

The alkylation of benzene with 1-methylcyclopentanol and 1-methyl-1-chlorocyclopentane has been studied in the presence of aluminum chloride. It has been demonstrated that these reactions proceed without noticeable isomerization, with formation of 1-methyl-1-phenylcyclopentane. A number of crystalline derivatives of 1-methyl-1-phenylcyclopentane have been obtained.

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9.5 g (18 %) of p-di-(1-methylcyclopentyl)benzene, which distilled at [illegible] (10 mm), [illegible] (from dilute alcohol).

According to the literature data, p-di-(1-methylcyclopentyl)benzene [illegible] [4].

The constants for 1-methyl-1-phenylcyclopentane were: b.p. [illegible]; MR 51.83; calculated 51.87.

Found %: C 90.06; H 9.90. $C_{12}H_{16}$. Calculated %: C 89.94; H 10.06.

The nitrocompound: m.p. 98°.

The alkylation of benzene with 1-methylcyclopentanol and 1-methylcyclopentene [illegible] in the presence of aluminum chloride. It has been demonstrated that these reactions [illegible] isomerization, with formation of 1-methyl-1-phenylcyclopentane. [illegible] 1-methyl-1-phenylcyclopentane [illegible].

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INTERACTION OF NICOTINE WITH METAL SALTS

II. THE INTERACTION OF NICOTINE WITH THIOCYANATE SALTS OF NICKEL, IRON (2+), COPPER (2+), MANGANESE, CADMIUM, AND ZINC

S. E. Burkat

In our preceding article [1], results on a study of the reaction between the cobalt thiocyanate complex and nicotine in aqueous solution were given. It was established that the reaction product represented a double salt of nicotine thiocyanate and of cobalt thiocyanate. The conditions of synthesis of this salt were developed, the composition and properties of this compound were studied, and it was demonstrated that it corresponded to the formula: $(C_{10}H_{14}N_2)_2 \cdot 2HCNS \cdot Co(CNS)_2$.

In previously published works [2,3], the authors noted that nicotine gives characteristic crystalline precipitates not only with cobalt thiocyanate, but with thiocyanate salts of other metals as well.

This given investigation was undertaken for the purpose of studying the composition and properties of reaction products between nicotine and nickel, iron (2+), copper (2+), manganese, cadmium, and zinc salts.

Experiments have shown that when nicotine, or its salts, is added to an aqueous solution of one of the above-enumerated metals, in the presence of ammonium thiocyanate, a crystalline precipitate forms, characterized by stability and by constant composition. Such compounds can be obtained with both pure preparations of nicotine and its salts with mineral acids, and with technical nicotine sulfate, or aqueous extracts of tobacco.

The products of interaction of nicotine with thiocyanate salts of the above-indicated metals represent crystalline substances slightly soluble in water, more readily so in hot water. They crystallize readily from water. The compounds obtained dissolve in dilute mineral acids, and again separate out from solution after neutralization with alkali. They dissolve in concentrated sulfuric and hydrochloric acids without any characteristic peculiarities. With the aid of standard reagents, the presence of the corresponding metal ions, thiocyanate ions and nicotine in saturated aqueous solutions of the compounds obtained by qualitative procedures is readily established. Aqueous solutions of these compounds are titrated with alkali, which indicates the presence of nicotine in their composition, in the form of a salt. The characteristics shown by the compounds obtained give grounds for considering them to be binary salts of nicotine thiocyanate, and thiocyanates of the above-cited metals. Analysis of the substances obtained has indicated that their composition can be represented by formulas (1) and (2):

$$N_2 \cdot 2HCNS \cdot Me(CNS)_2 \quad (1)$$

$$N \cdot HCNS \cdot Me(CNS)_2 \quad (2)$$

where N = an integer number for nicotine, Me = metal.

The compounds obtained are given in the table.

No.	Formula	Melting point*
1	$(C_{10}H_{14}N_2)_2 \cdot 2HCNS \cdot Ni(CNS)_2$	237-238°
2	$(C_{10}H_{14}N_2)_2 \cdot 2HCNS \cdot Fe(CNS)_2$	200-201
3	$(C_{10}H_{14}N_2)_2 \cdot 2HCNS \cdot Cu(CNS)_2$	135-136
4	$(C_{10}H_{14}N_2)_2 \cdot 2HCNS \cdot Mn(CNS)_2$	207-208
5	$(C_{10}H_{14}N_2)_2 \cdot 2HCNS \cdot Cd(CNS)_2$	209-210
6	$C_{10}H_{14}N_2 \cdot HCNS \cdot Zn(CNS)_2$	180-181

* The compounds melt with partial decomposition

EXPERIMENTAL

1. Synthesis of Nicotine Thiocyanate and Nickel Thiocyanate Binary Salt

2.9 g of crystalline nickel nitrate $Ni(NO_3)_2 \cdot 6H_2O$ was dissolved in 5 ml of water. A solution of 3.1 g of ammonium thiocyanate in 5 ml of water was prepared in a separate container, and the two solutions were mixed. 3.25 g of nicotine (base) was placed in a 100 ml flask, 20 ml of water added, and the resulting solution neutralized with 25% hydrochloric acid solution (indicator — methyl red). A solution of the nickel thiocyanate complex was added to the prepared nicotine solution, with vigorous stirring, and the mixture left for 15 minutes. The resulting precipitate was filtered off with suction, washed with 5-10 ml of water on the filter, and dried at 60°. The yield of resulting precipitate was 90% of theory, assuming that the reaction proceeded according to the following equation:

$$2C_{10}H_{14}N_2 \cdot HCl + Ni(NO_3)_2 \cdot 6H_2O + 4NH_4CNS = (C_{10}H_{14}N_2)_2 \cdot 2HCNS \cdot Ni(CNS)_2 + 2NH_4NO_3 + 2NH_4Cl + 6H_2O.$$

The resultant product was twice recrystallized from boiling water (the first time from 120 ml, and the second time from 100 ml). The crystalline powder was blue in color and without odor. The solubility in water at 20° was 0.60%. An aqueous solution was faint blue in color.

Quantitative determination of the metal, the thiocyanate ion and the nicotine was carried out according to standard analytical procedures.

0.3010, 0.3000, 0.4040 g substance. Found %: Ni 9.64, 9.16, 9.24; CNS' 36.61, 35.60, 35.15; nicotine 51.33, 51.78, 51.52. $(C_{10}H_{14}N_2)_2 \cdot 2HCNS \cdot Ni(CNS)_2$. Calculated %: Ni 9.50; CNS' 37.50; nicotine 52.47.

2. Synthesis of Nicotine Thiocyanate and Iron Thiocyanate Binary Salt

3.9 g of Mohr's salt and 3.1 g of ammonium thiocyanate were dissolved separately in 5 ml of water and the solutions were then mixed. 3.25 g of nicotine (base) was dissolved in a separate container, the resultant liquid neutralized with hydrochloric acid, and the above-prepared iron thiocyanate complex added with vigorous stirring. The resulting crystalline precipitate was filtered with suction, washed on the filter with 5 ml of cold water, and dried at 60°. The yield of substance was 80%, calculating for the nicotine taken in reaction.

$$2C_{10}H_{14}N_2 \cdot HCl + FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O + 4NH_4CNS = (C_{10}H_{14}N_2)_2 \cdot 2HCNS \cdot Fe(CNS)_2 + 2(NH_4)_2SO_4 + + 2NH_4Cl + 6H_2O.$$

The resultant compound was recrystallized twice from boiling water (the first time from 50 ml of water, and the second time from 40 ml) and dried between sheets of filter paper at room temperature.

Lustrous crystals, light-brown in color. Solubility in water at 20°—1.95%. The aqueous solution was yellow in color.

0.5000, 0.3000, 0.5030 g substance: Found %: Fe 9.48, 9.80, 9.25; CNS' 35.80, 36.00, 36.45; nicotine 52.92, 53.14, 53.00. $(C_{10}H_{14}N_2)_2 \cdot 2HCNS \cdot Fe(CNS)_2$. Calculated %: Fe 9.10; CNS' 37.79; nicotine 52.76.

3. Synthesis of Nicotine Thiocyanate and Copper Thiocyanate Binary Salt

5 g of crystalline copper sulfate $CuSO_4 \cdot 5H_2O$ was dissolved in 20 ml of water, and 10 g of crystalline ammonium thiocyanate was added to the resultant solution. The solution was filtered. 3.25 g of nicotine (base) premixed with 20 ml of water and neutralized with 25% hydrochloric acid, was added with vigorous stirring to 10 ml of the filtrate. The resulting precipitate was filtered by suction, washed on the filter with 5-10 ml of water, and dried between sheets of filter paper at room temperature. The yield of resultant product was 75%, calculating on the basis of nicotine taken for reaction.

$$2C_{10}H_{14}N_2 \cdot HCl + CuSO_4 \cdot 5H_2O + NH_4CNS = (C_{10}H_{14}N_2)_2 \cdot 2HCNS \cdot Cu(CNS)_2 + (NH_4)_2SO_4 + 2NH_4Cl + 5H_2O.$$

Fine powder, green in color. The resultant salt was not very soluble in cold water. It decomposed partially on boiling with water, forming a precipitate of copper thiocyanate. Crystals did not separate from the supersaturated aqueous solution. The aqueous solution was green in color.

0.5000, 0.5032, 0.3000 g substance. Found %: Cu 10.16, 10.52, 10.91. Nicotine 51.30, 52.59, 52.42. $(C_{10}H_{14}N_2)_2 \cdot 2HCNS \cdot Cu(CNS)_2$. Calculated %: Cu 10.23; nicotine 52.12.

4. Synthesis of Nicotine Thiocyanate and Manganese Thiocyanate Binary Salt

1.9 g of crystalline manganese thiocyanate $MnSO_4 \cdot 2H_2O$ and 3.1 g of ammonium thiocyanate were dissolved separately in 5 ml of water, and the two solutions combined. 3.25 g of nicotine (base) was mixed in a separate container with 10 ml of water and the resultant mixture neutralized with 25% hydrochloric acid. Manganese thiocyanate was added to the prepared nicotine solution with vigorous stirring, and the mixture left for 30 minutes. The crystalline precipitate was filtered off by suction and dried at 60°. The yield of compound was 84%, calculating on the basis of nicotine taken for reaction:

$$2C_{10}H_{14}N_2 \cdot HCl + MnSO_4 \cdot 2H_2O + 4NH_4CNS = (C_{10}H_{14}N_2)_2 \cdot 2HCNS \cdot Mn(CNS)_2 + (NH_4)_2SO_4 + 2NH_4Cl + 2H_2O.$$

The resultant compound was recrystallized twice from boiling water (the first time from 20 ml of water, the second time from 10 ml), and the crystals were dried between sheets of filter paper at room temperature.

A crystalline powder, light-yellow in color. Solubility in water at 20° – 4.4%. The aqueous solution was almost colorless.

0.5000, 0.3000, 0.4998 g substance. Found %: Mn 8.26, 8.13, 8.46; CNS' 35.50, 36.16, 36.54; nicotine 52.30, 52.69, 52.48. $(C_{10}H_{14}N_2)_2 \cdot 2HCNS \cdot Mn(CNS)_2$. Calculated %: Mn 8.96; CNS' 37.80; nicotine 53.01.

5. Synthesis of Nicotine Thiocyanate and Cadmium Thiocyanate Binary Salt.

1.84 g of anhydrous cadmium chloride, and 3.1 g of ammonium thiocyanate were separately dissolved in 5 ml of water and the solutions mixed. The resulting solution was poured, with vigorous stirring, into 3.25 g of nicotine (base) in 10 ml of water, neutralized beforehand with 25% hydrochloric acid. A light-yellow crystalline precipitate separated. The mixture was allowed to stand for 30 minutes, and the crystalline mass then filtered off by suction and dried at a temperature of 60°. The resultant compound was 86% of theoretical, assuming that formation of the compound occurred according to the following equation:

$$2C_{10}H_{14}N_2 \cdot HCl + CdCl_2 + 4NH_4CNS = (C_{10}H_{14}N_2)_2 \cdot 2HCNS \cdot Cd(CNS)_2 + 4NH_4Cl.$$

The resultant compound was recrystallized twice from boiling water (the first time from 100 ml of water, and the second time from 70 ml), and the crystals were dried between filter paper sheets at room temperature.

A white crystalline powder with yellow shade. Solubility in water at 20° – 0.80%. The aqueous solution was colorless.

0.5000, 0.3000, 0.5018 g substance. Found %: Cd 17.20, 16.46, 16.24; CNS' 32.98, 32.76, 33.12; nicotine 48.30 48.44, 48.39. $(C_{10}H_{14}N_2)_2 \cdot 2HCNS \cdot Cd(CNS)_2$. Calculated %: Cd 16.76; CNS' 34.60; nicotine 48.32.

6. Synthesis of Nicotine Thiocyanate and Zinc Thiocyanate Binary Salt

2.9 g of crystalline zinc sulfate $ZnSO_4 \cdot 7H_2O$ was dissolved in 5 ml of water. A solution of 3.1 g of ammonium thiocyanate in 5 ml of water was prepared in a separate container and the two solutions combined. 3.25 g of nicotine (base) was mixed in a porcelain cup with 10 ml of water and neutralized with 25% hydrochloric acid; the prepared complex solution of zinc thiocyanate was added with stirring to the neutralized nicotine solution. A thick, milky-white turbidity formed, from which there separated out a resinous mass, yellow in color. The liquid was poured off as thoroughly as possible and the resultant mass washed with 10 ml of cold water, and then dissolved in 120 ml of water by boiling, and the solution filtered immediately. Upon cooling, there separated out from the filtrate colorless silky needles. The resultant crystalline mass was repeatedly recrystallized from 80 ml of boiling water, and the crystals dried between filter paper sheets at room temperature. The yield of pure product was 45%, calculating on the basis of nicotine taken for reaction.

$$C_{10}H_{14}N_2 \cdot HCl + ZnSO_4 \cdot 7H_2O + 3NH_4CNS = C_{10}H_{14}N_2 \cdot HCNS \cdot Zn(CNS)_2 + (NH_4)_2SO_4 + NH_4Cl + 7H_2O.$$

Light, feathery, crystalline mass, white in color, with silky sheen. Solubility in water at 20° – 0.80%. The aqueous solution was colorless.

0.5000, 0.5014, 0.3000 g substance. Found %: Zn 16.46, 16.43, 16.25; CNS' 40.00, 41.28, 41.42. nicotine 41.00, 41.14, 41.48. $C_{10}H_{14}N_2 \cdot HCNS \cdot Zn(CNS)_2$. Calculated %: Zn 16.22; CNS' 43.24; nicotine 41.00.

SUMMARY

Binary salts between nicotine thiocyanate and the thiocyanates of nickel, iron (2+), copper (2+), manganese, cadmium, and zinc have been synthesized. The composition, properties, and formulas of the compounds obtained are given in the text of the article.

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* See Consultants Bureau Translation, p. 165.

[illegible]

A crystalline powder, light yellow in color. Solubility in water at 20° [illegible]. The aqueous solution was almost colorless.

[illegible] g substance: Found %: [illegible]

[illegible]

4. Synthesis of Nicotine Thiocyanate and Cadmium Thiocyanate Double Salt

1.84 g of anhydrous cadmium chloride, and [illegible] g of ammonium thiocyanate were dissolved [illegible] ml of water and the solutions mixed. The resulting solution was [illegible] nicotine (base) in [illegible] ml of water [illegible] precipitate separated. The mixture was allowed to stand [illegible] off by suction and dried at a temperature of 60°. The resulting compound [illegible] formation of the compound [illegible] according to the following scheme:

[illegible]

The resulting compound was recrystallized [illegible] the second time from [illegible] and the crystals were dried between filter paper [illegible]

A white crystalline powder with yellow shade. [illegible] The aqueous solution was colorless.

[illegible] g substance: Found %: [illegible]

[illegible]

5. Synthesis of Nicotine Thiocyanate and Zinc Thiocyanate Double Salt

[illegible] of crystalline zinc sulfate [illegible] was dissolved in 5 ml of water. A solution of [illegible] of ammonium thiocyanate in 5 ml of water was prepared in a separate [illegible], and the two solutions combined. [illegible] g of nicotine (base) was [illegible] A thick, milky-white [illegible] formed [illegible] The liquid was sucked off as thoroughly as possible and the [illegible] washed with 10 ml of cold water, [illegible] then dissolved in 120 ml of water at boiling, [illegible] of boiling water, and the crystals dried between filter paper [illegible]

[illegible]

Light, feathery, crystalline mass, white in color. [illegible] The aqueous solution was colorless.

[illegible] g substance: Found %: [illegible]

[illegible]

SUMMARY

Double salts between nicotine thiocyanate and the thiocyanates of [illegible] have been synthesized [illegible] are given in the text of the article.

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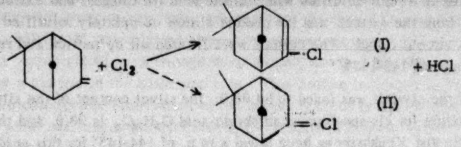
* See Consultants Bureau Translation [illegible]

NEW TYPES OF TERPENE TRANSFORMATIONS

XV. THE ACTION OF CHLORINE UPON β-FENCHENE

D. Tishchenko and S. Sheina

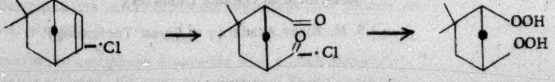
In article I [1], the authors developed a general concept for predicting the structures of unsaturated chloroterpenes which should be formed by the interaction of chlorine with any terpene. Additional ideas on the subject were given in subsequent articles XI and XIV [2]. In accordance with these, it could be foreseen that the interaction of chlorine with β-fenchene would be expressed by the following scheme (the saturated dichloride is not presented):



The possibility of forming the chloride (II) is explained by the same causes as for the corresponding chlorides of camphene and α-fenchene [2]. The reaction of chlorine with β-fenchene has not been studied by anyone, and the accuracy of our assumptions could only be verified experimentally.

β-Fenchene was synthesized according to the method of Qvist [3], by dehydrating fenchilic alcohol with potassium acid sulfate, and separated from the accompanying γ-fenchene by fractionation on an effecient column. Its constants corresponded to the literature data.

Chlorination of β-fenchene was carried out under conditions described many times. By distilling the reaction products, monochloroterpene was isolated, boiling within a narrow range, which indicated the absence of isomeric chlorides with various (primary, secondary, and tertiary) position of the chlorine atom. Not all the chlorine (16.9% out of the 20.4%) was found to be mobile, and the molecular refraction of the monochloroterpene exceeded that calculated for chloride (I) by 0.3, which should be attributed to the presence of about one-fourth chloride (II) in the chloroterpene. Upon ozonizing the chloroterpene, chloroketoaldehyde resulted, which upon further oxidation, gave cis-apo-fenchocamphoric acid, which ensured the structure (I) as the principal constituent of the chloroterpene:



Thus, it can be considered that the authors' predictions regarding the interaction mechanism of chlorine with β-fenchene are confirmed by experimental data, and that this mechanism does not differ from that for other terpenes.

EXPERIMENTAL

Synthesis of fenchilic alcohol has been described by the authors [2]. Its dehydration was carried out under the conditions of Quist [3]. The mixture of fenchenes was fractionated on a column with an efficiency of about 40 theoretical plates, with 15-16 phlegm number, in order to obtain sharply boiling fractions (pressure 10 mm), for which purpose three distillations were necessary. γ-Fenchene was isolated in a yield of 39%, β-fenchene in yield of 34% of the charge. Constants for the β-fenchene: b.p. 43° (at 10 mm); d_4^{20} 0.8654; n_D^{20} 1.4692; MR_D 43.90. Calculated for β-fenchene, 43.91.

Chlorination of β-Fenchene

50 g of fenchene, 30 g of $NaHCO_3$, 12.5 g of $KMnO_4$ and 70 ml of HCl (sp. gr. 1.17). Cl' found in the salts and in the trap was 5.15 g, chlorine in the organic portion was 7.6 g, the percentage abnormal reaction being 80. The reaction product was fractionated on a column of 6-7 plates, at a phlegm number of 15-16 and at a pressure of 8 mm. 17 g of monochloroterpene resulted, with the constants: b.p. 40-42°; d_4^{20} 1.0128; n_D^{20} 1.49165: % Cl 20.4; % allyl chlorine 16.9.

Ozonization of Chloroterpene

5 g of chloroterpene in 5 ml of chloroform was ozonized with ice-cooling (44 liters of 2.4% ozone being consumed), to a negative reaction to bromine. The ozonide solution was stirred with water for 6 hours, the chloroform layer separated, and the chloroform removed from it, weight of the residue being 6.1 g. About 6.0 g of the chloroketoaldehyde may have resulted. The residue was distilled under a pressure of about 1.10^{-3} mm. Most of the fraction distilled off at a bath temperature of about 180°. For it was found: d_4^{20} 1.129; n_D^{20} 1.4902.

Found %: C 59.1, H 7.8. $C_{10}H_{15}O_2Cl$. Calculated %: C 59.2, H 7.5.

Oxidation of Chloroketoaldehyde

4% permanganate solution was added to 2.4 g of the substance in 50 ml of acetone, and 30 ml of water, to a stable pink coloration (140 ml). The manganese dioxide was extracted three times with boiling water, the combined filtrates evaporated to 50 ml, acidified with sulfuric acid (to Congo), and extracted repeatedly with ether. Ether was removed from the extract, and the residue almost completely solidified to a mush of needle crystals saturated with a viscous liquid. The crystals were filtered off by suction and recrystallized from aqueous alcohol to a constant m.p. of 142-143°.

The equivalent weight of the crystals was found to be 93.9; the silver content of the silver salt was found to be 54.2%. The equivalent weight for cis-apo-fenchocamphoric acid $C_9H_{14}O_4$ is 93.0, and the percent silver of the silver salt 54.0. Nametkin and Khukhrikova have found a m.p. of 144-145° for this acid [4].

SUMMARY

The reaction of chlorine with β-fenchene has been investigated. The principal product has been found to be the chloro-γ-fenchene (I), and a side-product, apparently ω-chloro-β-fenchene (II), which is in agreement with the reaction mechanism of chlorine with terpenes proposed earlier by the authors.

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[3] Qvist. Ann., 417, 278 (1918).

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* See Consultants Bureau Translation, p. 593.

** See Consultants Bureau Translation, p. 1863.

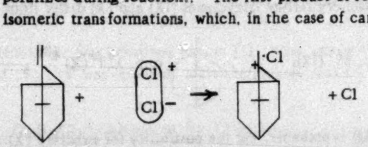
*** See Consultants Bureau Translation, p. 1051.

NEW TYPES OF TERPENE TRANSFORMATIONS

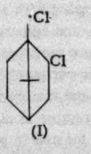
XVI. THE STRUCTURE AND CERTAIN TRANSFORMATIONS OF CAMPHENE DICHLORIDE

D. Tishchenko and I. Uvarov*

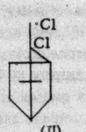
In one of the preceding articles are given the results of a study of the interaction between chlorine and camphene, and the structures of the resulting monochloroterpenes were established at that time [1]. Up to the present time the authors have not investigated the structures of terpenes of the saturated dichlorides, products of the "classical" reaction which result upon chlorination. However, this process in not inactive. From both the scanty experimental data to be had in the literature on this subject, and the more extensive information on the interaction of terpenes with polar or polarizing substances at the time of reaction, do not make allowance for a consideration that addition of two chlorine atoms to a terpene molecule will proceed in any number of cases in accordance with a "principle of least change in structure", nor that the terpene double bond will be saturated with chlorine without a change in the basic structure. Thus Aschan indicated [2] that α-pinene dichloride has the structure of 2,6-dichlorocamphane (conversion of the pinane nucleus to the camphane nucleus). With the analogous retropinacolinic acid, rearrangement proceeds with addition of organic acids to camphene to form esters of isoborneol possessing the camphane nucleus. In a similar fashion, proceeds the addition of hydrogen halide to α- and β-pinenes. At the same time, the action of non-polar reagents, for example of ozone and hydrogen, does not lead to resynthesis of the terpene nucleus. The organic acids and hydrogen halides are without doubt polar reagents. The chlorine atom is formally non-polar, but the authors, and other investigators (see preceding articles) have accepted the fact that it polarizes during reaction.. The first product of reaction should be the carbonium cation, capable of undergoing isomeric transformations, which, in the case of camphene, can be represented by the equation:



The chlorine anion can pull off one or more protons [1], or add to the cation, before or after its isomerization. If based upon the analogy of organic acid addition to camphene, then the camphene dichloride should be in the form of 2,10-dichlorocamphane (I) (retropinacolinic regrouping). and not the "normal" camphene dichloride (II).



(I)



(II)

A solution of this reaction process is possible only through the experimental procedure.

Interaction of camphene dichloride with a large excess of sodium in ether solution, followed by subsequent decomposition of the reaction product with aqueous alcohol, gave a mixture of hydrocarbons with a predominance of camphane, containing in addition a new tricyclene (m.p. 110-111°) and some bornylene.

Synthesis of camphane and of bornylene indicated that camphene dichloride has the neucleus of camphane, and not of isocamphane, and that structure (I) is more probable for the dichloride. A study of the dichloride interaction with sodium in moist ether also led to the same results The removal of one molecule of hydrogen chloride from camphene dichloride of structure (II) can give either the chloride of tricyclene (III) or ω-chlorocamphene (IV) :

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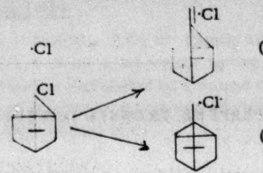
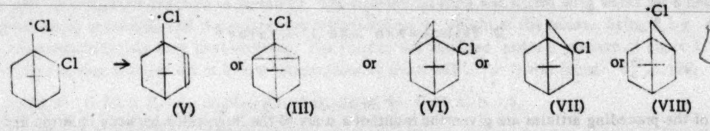
* The experimental work was carried out by I. Uvarov, member of the students scientific society at the Department of Organic Chemistry, Academy of Wood Technology.

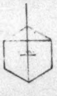


The dichloride (I) will give either chlorobornylene (V), or chlorotricyclene (III), or the chloride of neotricyclene (VI), (VII) and (VIII).

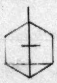


Camphene dichloride does not react in a boiling solution of potassium hydroxide in ethanol, nor does it react with the solution in butyl alcohol if azeotropic removal of the evolving water is assured. A mixture of monochloroterpenes is formed in good yield, consisting of not less than 90% of crystalline chloroterpenes, with m.p. 23-24°, non-oxidizable by potassium permanganate and non-ozonizable by addition to the unsaturated chloroterpene. The monochlorides (III) and (IV) are liquids and are therefore excluded; also excluded is the chloride (V) (which should oxidize and ozonize); formulas of the structures (VI), (VII), and (VIII) are left for investigation. The melting point of this crystalline chloroterpene does not coincide with any of the known chloroterpenes.

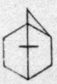
This crystalline chlorotricyclene reacts readily in ether solution with magnesium, with activated ethyl bromide, and gives the corresponding organomagnesium compound in yield not less than 70%. Upon decomposing the organomagnesium compound with water, a crystalline terpene resulted with m.p. 110-111°, non-oxidizable with water and acetone solutions of permanganate, and differing from bornylene in having a sharp melting point at 112-113°. In admixture with bornylene, it melted without depression but this phenomenon is observed in a number of cases with terpene chemistry. From its non-oxidizability with permanganate, this terpene should be some kind of tricyclene. The known crystalline tricyclenes (IX) and (X) differ from ours in melting points:



m.p. 68° (IX);



m.p. 117° (X) [3] ;

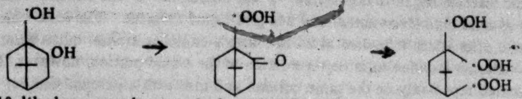


(XI) .

The formula for structure (XI) is probable, but the possibility for structure (X) is not excluded. Upon hydration according to the method of Konovalov-Bertran-Walbaum, terpene (X) should produce epiborneol, with m.p. 186°, and terpene (XI) can give either the neoborneol of Akhmatovich with m.p. 186° [4], or borneol with m.p. 202°, or isoborneol with m.p. 212°, or 10-hydroxycamphane.

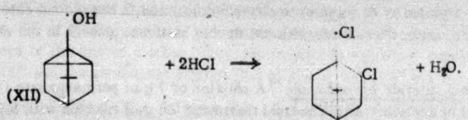
In actuality, the alcohol with a m.p. of 186° resulted. Neoborneol of Akhmatovich gives camphor with m.p. 176° upon oxidation, and epiborneol gives epicamphor with m.p. 180°. Hence, both of these alcohols and their ketone derivatives are indistinguishable from each other. The oxime of camphor melts at 117°, the α-bromocamphor at 76°; the corresponding derivatives of epicamphor melted at 94 and 133°. The oxime of our camphor melted at 117°, and the bromoderivative at 74-76°; hence, our alcohol was found to be neoborneol, and our terpene has the structure of neotricyclene (XI). Synthesis of neotricyclene (XI) from camphene dichloride indicated that chlorine is located in position 2 or 10 in the latter compound; the positions of the other chlorine atoms removed by hydrogen exchange upon decomposition of the organomagnesium compound with water remain unknown.

Oxidation of the organomagnesium compound by oxygen gives a terpene alcohol $C_{10}H_{16}O$ with m.p. 158-160° differing in melting point from that of any known terpene alcohol. This was a secondary alcohol, since it could be oxidized to the corresponding ketone, with a m.p. of about 143°, and since it did not react with phthalic anhydride in boiling benzene, but reacted in boiling xylene to form the phthalate, melting at 104-105° (phenylurethane with m.p. 94-95°); consequently structure (VII) is eliminated. The semicarbazone of the ketone melted at 208-209°, and was distinguished by its melting point from the semicarbazones of ketones $C_{10}H_{14}O$. Upon hydrogenation, the authors' new alcohol gave the corresponding diol $C_{10}H_{18}O_2$, which could be oxidized to the ketopinic and carboxyapocamphoric acids, which is feasible only for the structure 2,10-dihydroxycamphane:



This 2,10-dihydroxycamphane melted at 172-178°, and was distinguished by its melting point from the known dihydroxycamphanes (2,6- 240-242°, 2,5- 233-234°, 2,3- 230-231°). By the same fact, the camphene dichloride possessed the structure (I), of 2,10-dichlorocamphane.

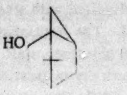
There is described in the literature a dichloride accepted for 2,10-dichlorocamphane, the Komppa dichloride with a m.p. of 58°, obtained by the action of hydrogen chloride upon tricyclene (XII) [5]:



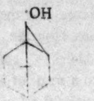
(XII)

This dichloride by the synthetic method could have the structure (I), and in such case should be the stereoisomer of our camphene dichloride. Of course, a final solution to the problem of the structure of the Komppa dichloride can only be found from the experimental approach, perhaps even by the conversions developed by the authors.

The neotricyclenol obtained by the authors, with m.p. 158-160°, may have the structure (XIII) or (XIV):



(XIII)



(XIV)

Its structure was not proved by the authors, due to a lack of time, but it can be proved by oxidation of the alcohol; upon oxidation with permanganate, the alcohol (XIII) should give a dicarboxylic acid, the alcohol (XIV) should give a ketopinic acid, and from it the carboxyapocamphoric acid.

EXPERIMENTAL

Synthesis of camphene dichloride was described earlier [1]. After two or three recrystallizations from methanol or ethanol, a m.p. of 133-134° was obtained, which remained constant after subsequent recrystallizations.

Found %: Cl 34.4, 34.4. $C_{10}H_{16}Cl_2$. Calculated %: Cl 34.3.

Synthesis of Chloroneotricyclene

675 g of dichloride was heated to boiling with a solution of 280 g of potassium hydroxide in one liter of butanol. The reflux condenser was connected with the reaction flask through a water trap. 55 ml of water had separated after 20 hours. The flask contents were mixed with 1 liter of water, the oily layer removed, washed with weak hydrochloric acid, dried with potash, and fractionated on a column with 7-8 theoretical plates of phlegm number 8-10 at 8 mm pressure. After distilling off the butanol, there resulted 266 g of fraction with b.p. 77-79° (the monochloride), 52 g of an intermediate fraction, 79-90°, and 250 g of camphene dichloride. The latter was treated for a second time with potassium hydroxide in butanol. After a final fractionation, 431 g of monochloride resulted with m.p. 77-79° at 8 mm.

Standard bromine solution was added to weighed portions of the monochloride in the amounts of 0.5193 and 0 4368 g, dissolved in chloroform and cooled with snow, to a permanent color; the amount of bromine used was 0 03290 g and 0.0278 g, respectively, which corresponded to a content of about 7% monochloride with double bond, in the fraction.

50 g of the monochloride fraction was ozonized in carbon tetrachloride with 5% ozone passed through, calculated on the basis of one double bond in the monochloride. After decomposition of the ozonide solution with water, and fractionation of the reaction products, it was found that at least 70% of the initial monochloride failed to react with the ozone. Analysis of the monochloride gave:

d_4^{12} 1.035; n_C^{12} 1.4884; MR_C 47.29; $C_{10}H_{15}Cl\Delta$. Calculated 47.12.

0.2010 g substance: 0.1655 g AgCl. 0.2333 g substance: 0.1941 g AgCl. Found %: Cl 20.6, 20.8. $C_{10}H_{15}Cl$. Calculated %: Cl 20.7.

Upon cooling to +11°, the fraction began to crystallize. It was cooled to −8° and filtered with vacuum at the same temperature. 188 g of solid chloride resulted, and 240 g of liquid chloride. The solid chloride was pressed off at room temperature, after which it melted at 24-25°, with a camphor aroma, quite volatile. Its chloroform solution did not decolorize bromine solution; a solution of the liquid portion, however, decolorized. The liquid portion was fractionated repeatedly on the same column at 8 mm with a phlegm number of 15-16. 15 g of fraction was collected with a b.p. of 31-77°, the main fraction being 77-79°, solidifying at −8°. 132 g of the solid chloride was removed and 77 g of the liquid portion which solidified partially at −23°. 320 g of solid chloride resulted, melting at +20°.

Oxidation of solid and liquid monochlorides. Weighed portions of 0.1464 g and 0.2894 g, respectively, were dissolved in acetone, to which was added 1% acetone solution of potassium permanganate. In the first case, 0.2 ml was added over a period of 52 minutes to a stable color, and in the second case, 2.2 ml over a period of 120 minutes. Hence, about 2% chloride with one double bond was present in the solid chloride, and in the second, about 13%.

Purification of the liquid chloride by oxidation. A solution of 7 g of permanganate in acetone was added to 77 g of chloride in 100 ml of acetone. After the usual treatment, 65 g of fraction with b.p. 77-78° at 8 mm resulted, which solidified completely at −8°. After pressing out on paper, m.p. 23-24°.

Synthesis of Camphane and Bornylene from Camphene Dichloride

10 g of sodium in a thin ribbon was put into 400 ml of dry ether, and 20 g of the dichloride added slowly through a reflux condenser. The flask was heated to the boiling point of ether for 20 hours, and the alcohol was then added slowly to dissolution of sodium excess, and the flask contents distilled with steam. The ether layer of the distillate was separated, dried with calcium chloride, and fractionated. The fraction with b.p. 145-160° solidified completely in the cooler, its m.p. 110-114°, and did not contain chlorine. Half of the fraction (3.7 g) was recrystallized three times from alcohol to a m.p. of 151-154°, the fourth crystallization not changing the melting point. The second half was heated with 20 ml of sulfuric acid at 100°. The crystals which sublimed into the reflux condenser (1.5 g) had a m.p. of 148-150° (in a sealed capillary), and after two recrystallizations from alcohol, an unchanging m.p. of 153.5-154°.

0.1150 g substance: 0.3666 g CO_2; 0.1356 g H_2O. Found %: C 86.9; H 13.1. $C_{10}H_{18}$. Calculated %: C 87; H 13.

A hydrocarbon was isolated from the alcoholic mother liquors, which melted from 100 to 113°. 1.85 g of hydrocarbon in 5 ml of benzene was heated to boiling in a flask with reflux condenser with a solution of 5.7 g of permanganate in 570 ml of water for 16 hours, after which the large unreacted excess permanganate was decomposed with hydrogen peroxide, the manganese dioxide removed with suction, the alkaline solution evaporated to 20 ml, and acidified (to Congo), followed by extraction with ether. Ether was removed from the extract, the small crystalline residue was recrystallized from hot water. 0.3 g of needle crystals resulted, with m.p. 200-201°, and the gram-equivalent of 100.1 corresponded to camphoric acid.

Proof of the presence of neotricyclene in the products of interaction of camphene dichloride with sodium.

94 g of camphene dichloride was dissolved in 400 ml of dry ether, and 22 g of sodium in thin strips was gradually introduced into the solution. After 23 hours, all of the sodium had reacted. 400 ml of water was introduced into the flask, the ether layer removed, dried, and fractionated. The fraction with b.p. 145-170° solidified in the cooler (22.6 g). It was rolled over paper to evaporate the readily-volatile camphane, the weight of the residue being 12.1 g, which was oxidized in an acetone solution of 2.5 g of permanganate, after which procedure the acetone was distilled off, and from the distillate the hydrocarbon which distilled off with the acetone precipitated (8.0 g, m.p. 90-98°). These 8 grams were dissolved, with heating, in 15 ml of alcohol, and upon cooling, 5 g of feathery crystals precipitated, which melted, after prolonged drying over potassium hydroxide, at 104-106°. On hydrogenation of these crystals (see below), neoborneol resulted, with m.p. 186-187° (m.p. of the phenylurethane was 139-140°).

The Interaction of Chlorotricyclene (m.p. 23-24°) with Magnesium

80 g of magnesium shavings was placed in a flask, equipped as usual, and covered with ether, after which 20 g of chloride was introduced, an iodine crystal, and 1 g of ethyl bromide; after start of the reaction, a solution of 20 g of ethyl bromide and 300 g of the chloride in 500 g of dry ether was added over a period of 5 hours, with stirring and water cooling, after which mixing was continued for another 5 hours. From an aliquot portion of the solution titrated, 1.33 g-equiv. of organomagnesium compound was found, the yield being 71%. The solution was decanted off from the excess magnesium, the magnesium washed with ether, and the solution combined, to a total volume of 1250 ml.

500 ml of this solution was dissolved in water, the ether layer separated, and the ether removed from it, the weight of residue being 87 g. The ether was distilled, the residue dried with powdered potassium hydroxide, and distilled in a fractionating column. From the residue there was obtained 4.5 g of neotricyclene, with m.p. 108-110°. It was volatile with vapors of moist ether.

87 g of residue was fractionated. There was obtained: to 146° 3.3 g; 146-148.5° (160)° 41.8 g; 160-235° 11.2 g; residue 29.8 g. 4.5 g of neotricyclene (see above) was added to the main fraction and 33.3 g (see below) and 79.6 g were fractionated. Result: I) 146-147.5°, 12.2 g, b.p. 108-112°; II) 147.5-148.5° 38.1 g, b.p. 108-111°; III) 148.5-160°, 10.2 g, m.p. 85-103°; IV) 160-235° 11.2 g; residue 18.4 g. Fraction II distilled almost completely at 148.5° upon the second distillation. With the same fractionating set-up and thermometer, known bornylene (m.p. 104-106°) distilled at 146°. 15.7 g of Fraction II did not dissolve in 40 ml of alcohol in the cold, but dissolved upon boiling. After cooling, 8 g of feathery crystals precipitated, m.p. 110-112°, after drying over alkali. Several drops of water was added to the heated mother liquor, the crystals (2.7 g) which precipitated in the cold, melting, after drying, at 110-112°, and the subsequent crystals (3.1 g) also at 110-112°, the last precipitate (0.7 g) at 96-102°.

0.1311 g substance: 0.4254 g CO_2; 0.1404 g H_2O. Found %: C 88.5; H 11.9. $C_{10}H_{16}$. Calculated %: C 88.3; H 11.7.

The terpene contained a small impurity of unsaturated hydrocarbon: 15.5 g of Fraction II was dissolved in 50 ml of pure acetone, and to the solution was added a 1% acetone solution of permanganate; very rapid reduction occurred up to 17 ml, then more slowly, and at 24 ml there was no decolorization after 20 minutes. The manganese dioxide was filtered off with suction, the solution diluted with water, the terpene filtered off suction, dried over potassium hydroxide, and distilled from the flask through a fractionating column. It distilled almost completely at 148-148.5°, m.p. 110-111°. At the same time, the oxidizability of bornylene was verified by the Meerwein method [6]; the weighed portion was 0.598 g, which reduced rapidly 38 ml, the experiment then being terminated.

The residue from the first distillation (18.4 g) was fractionated at 13 mm, and distilled almost completely at about 180°, solidifying completely in the container. After three recrystallizations from ethanol, a stable m.p. was attained, 78-79°.

0.1002 g substance: 0.3273 g CO_2; 0.1010 g H_2O. Found %: C 89.1; H 11.2. $(C_{10}H_{15})_2$. Calculated %: C 88.9; H 11.1

The substance in acetone solution did not reduce the permanganate. It was recognized as dineotricyclenyl.

750 ml of an ether solution of the organomagnesium compound was oxidized with oxygen, 20 liters of oxygen being absorbed, the absorption then slowing down sharply. The reaction product was decomposed with water and weak acetic acid to a neutral reaction to litmus, the ether layer removed, dried with potash, and the ether distilled in a column of 8-10 theoretical plates, weight of the residue being 183 g. From this 33.3 g of neotricyclene was sublimed at 15 mm, and added to the above synthesized. The residue was distilled at 17 mm, the main fraction boiling at 100-102°, solidifying immediately in the container (alcohol); the next narrow fraction boiled at 172-175° at 15 mm, solidifying completely in the receiver, and after a double recrystallization from alcohol, melted at 78-79°, (dineotricyclenyl).

Fraction 100-102° at 17 mm was filtered off with suction from a small quantity of liquid, white crystals with camphor aroma, m.p. 132-145°, quite readily dissolved by all organic solvents, for example, 69 g dissolved in 15 ml of ethyl alcohol, and did not crystallize out upon cooling to −23°. Crystallization was successful from acetone or methyl acetate upon evaporation of the solvent by standing in open conical flasks; in the case of acetone, a constant m.p. was reached at 159-160°, and in the case of methyl acetate, 160-161°, long flat, lustrous needles.

0.1705 g substance: 0.3485 g CO_2; 0.1160 g H_2O. Found %: C 79.1; H 10.2. $C_{10}H_{16}O$. Calculated %: C 78.9; H 10.5.

Acid Phthalic Neotricyclenol Ester. The ester did not result in boiling benzene, the alcohol apparently not being primary; 2 g of the alcohol, 2 g of phthalic anhydride and 20 ml of xylene were heated for 2 hours at boiling temperature, water then added and the cooled reaction product neutralized with alkali to phenolphthalein. The aqueous layer was separated, filtered, and acidified with hydrochloric acid. A rapidly crystallizing oil resulted (3.8 g). The crystals dissolved completely in 50 ml of hot gasoline (b.p. 70-100°), needles resulting upon cooling. A third and fourth crystallization gave crystals with m.p. 104-105°.

0.1568 g substance: 5.23 ml 0.1 N alkali. Found: g-equiv. 301. $C_{18}H_{20}O_4$. Calculated: g-equiv. 300.

Phenylurethane of Neotricyclenol. 2 g of the alcohol and 4 g of phenylisocyanate were sealed together and heated for 7 hours at 80°, the excess of phenylisocyanate then being distilled off in vacuo, the solidified residue ground with water, and after 24 hours pressed out on paper and recrystallized from gasoline to an unchanging m.p. of 94-95° (hard prisms, four recrystallizations).

Hydrogenation of Neotricyclene. 32 g of the terpene with m.p. 110-111°, 80 ml of glacial acetic acid and 2 ml of 50% sulfuric acid were heated on a reflux (bath temperature 60°) to the cessation of terpene sublimation (6 hours). 20 ml of water was added to the reaction product, extraction with petroleum ether was carried out, followed by drying with potash and fractionation. 37.5 g of liquid fraction resulted with b.p. 117-118° at 23 mm. It was saponified by 6 hours boiling with an alcoholic (80 ml) solution of 15 g of potassium hydroxide; after dilution with water, the solid alcohol (28.1 g) was filtered off by suction and recrystallized from benzene. After a third recrystallization, there was attained a constant m.p. of 185.5-186°.

0.1151 g substance: 0.3295 g CO_2; 0.1233 g H_2O. Found %: C 78.1; H 11.9. $C_{10}H_{18}O$.
Calculated %: C 77.9; H 11.7.

In composition and melting point, the alcohol could be considered to be the neoborneol or the epiborneol.

Phenylurethane of the Alcohol. 1 g of the alcohol and 0.8 g of phenylisocyanate were sealed and heated for 1 hour on a boiling water bath. Everything solidified completely. After three recrystallizations from gasoline with b.p. 75-90°, there was obtained an unchanging m.p. of 138-139°. Melting point of the neoborneol phenylurethane was 140-141° [4], the epiborneol, 94-96° [7]. The alcohol can be considered to be neoborneol.

Oxidation of the Alcohol to the Ketone. 10 g of alcohol was dissolved in 100 ml of ether, and to this solution with water cooling and stirring there was added a solution of 4.5 g of chromic anhydride and 7 g of sulfuric acid in 60 ml of water; the ether and ketone were then flushed out with steam, and ether removed from the ether layer of the distillate, weight of the solid residue being 8.4 g. It did not give aldehyde reactions, was readily dissolved by all solvents, and after drying over sulfuric acid, gave an m.p. of 162-171°.

The Oxime of the Ketone. 1 g of the ketone, 1 g of hydroxylamine hydrochloride and 1 g of sodium hydroxide in 18 ml of alcohol were heated to boiling for 1 hour. The solution was then diluted with water and neutralized to phenolphthalein. The oxime was pressed out on paper and distilled with steam. The crystalline distillate in the condenser, after drying over sulfuric acid, melted at 98-110°. Two recrystallizations from alcohol raised the m.p. to 115-117°, a third did not change the melting point. The oxime of the camphor had an m.p. of 117°, the oxime of epicamphor an m.p. of 94°.

The bromoketone [8] was obtained from 3 g of the alcohol; after four recrystallizations from gasoline-ether mixture, an unchanging m.p. of 74-76° was attained. The m.p. of the bromocamphor was 76°, of the bromoepicamphor, m.p. 133°. The initial alcohol was found to be neoborneol. By the same fact structure (XI) was proven for the neotricyclene. Since the camphene dichloride, upon interaction with sodium, also gives the neotricyclene (XI), the structure 2,10-dichlorocamphene (see above) should be assigned to the dichloride.

Oxidation of Neotricyclenol to the Corresponding Ketone.

A solution of 7 g of chromic anhydride and 10.5 g of sulfuric acid in 57 ml of water was added to 11.5 g of the alcohol with m.p. 156-158° in 50 ml ether, with stirring and cooling. The reaction product was then flushed out with steam, and the residue (6.3 g) obtained from the ether layer of the distillate after drying with potash and removing the ether, was fractionated. 4.5 g of solid product, with b.p. 200-205°, resulted. After pressing out on paper and drying over solid potassium hydroxide, m.p. 142-144°. The substance had a camphor odor and was quite rapidly volatilized; it did not give aldehyde reactions. Its semicarbazone resulted by 2 hours of boiling with an alcoholic solution of semicarbazide acetate, and brought crystallization from benzene to a stable melting point of 208-209°.

Hydration of Neotricyclenol to Camphanediol-2, 10.

23 g of the alcohol with m.p. 156-158°, 60 ml of acetic acid and 1.5 ml of 50% sulfuric acid were heated on a boiling water bath for 6 hours, and then after diluting with water to 300 ml, unreacted alcohol was distilled out of the solution with steam, 3.5 g was distilled, m.p. 152-158°.

The aqueous solution was evaporated in vacuum to 100 ml, crystals and oil resulting, crystals (13.5 g) not neutralizing alkali upon boiling, the oil (4 g) neutralizing. Evidently, upon distilling with steam in the presence of sulfuric acid, the dioldiacetate saponified completely. The oil was saponified by boiling with alkali, the reaction product solidifying. It, and the first crystals, were crystallized separately from the aqueous solution to an unchanging m.p. of 172-173° (four recrystallizations).

0.1286, 0.1265 g substance: 0.3327, 0.3266 g CO_2; 0.1246, 0.1221 g H_2O. Found %: C 70.6, 70.4; H 10.8, 10.8. $C_{10}H_{18}O_2$. Calculated %: C 70.6; H 10.6.

Oxidation of Camphanediol-2,10. 2.6 g of the diol in 300 ml of water was oxidized on a boiling bath by addition of a 3% solution of permanganate to a pink color stable for 30 minutes. 315 ml, i.e., about 9.45 g of $KMnO_4$ was used. The manganese dioxide was filtered off with suction, the alkaline solution evaporated to 50 ml and acidified with hydrochloric acid to Congo red. 1.38 g of crystals (hard prisms) resulted, with m.p. 207-210°, and an equivalent weight of 185 (0.0848 g of substance, 4.57 ml of 0.1 N alkali). By repeated crystallizations from aqueous alcohol, it was possible to bring the melting point to 217-219°, equivalent weight 183 (ketopinic acid, m.p. 232°, equivalent weight 182). Since ketopinic acid gives carboxyapocamphoric acid, of m.p. 199-201° and equivalent weight 76.6, with nitric acid (sp. gr. 1.40), all fractions, including the crystallized 1.38 g of primary precipitate, and the 1.25 g of acids, with m.p. 198-206°, extracted with alcohol from the mother liquor from the first precipitation, were heated with 20 ml of nitric acid (sp. gr. 1.40) to cessation of nitrogen oxide evolution (12 minutes). 1.45 g of needle crystals precipitated from the cooled solution. They were filtered off by vacuum, washed with a small quantity of water, and dried at 100° to constant weight. M.p. 199-201°, with the evolution of carbon dioxide, equivalent weight 75.7 (0.0614 g of the substance, 8.1 ml of 0.1 N alkali). The acid was found to be the carboxyapocamphoric.

SUMMARY

1. The structure of camphene dichloride has been studied, and it has been demonstrated to be 2,10-dichlorocamphane. Its formation from camphene proceeds with retropinacolinic rearrangement, which permits a deduction relative to polarization of the chlorine molecule at the moment of its reaction with the double bond of camphene.

2. Upon interaction with excess sodium, 2,10-dichlorocamphane gives camphane, neotricyclene (XI) and some bornylene.

3. Removal of a hydrogen chloride molecule from 2,10-dichlorocamphane at the present time indicates a chloride of either neotricyclene (VI), or of (VIII).

4. Decomposition of the organomagnesium compound from (VI) or (VIII) with water gives neotricyclene (XI), unknown up to the present time, and oxidation of the organomagnesium compound with oxygen gives a new tricyclic alcohol, with m.p. 159-160°.

5. Hydration of this alcohol gives camphanediol-2,10, not described until now.

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[illegible] m.p. of 176–177° [illegible]

[illegible] g substance: [illegible] g CO_2; [illegible] g H_2O. Found %: [illegible]

[illegible] Calculated %: [illegible]

Oxidation of Camphenonol-6 (I). 3.0 g of the [illegible]

[illegible]

SUMMARY

1. The [illegible] camphenonol [illegible]

[illegible]

[illegible] single bond of camphene.

2. [illegible]

3. [illegible]

4. [illegible]

5. [illegible]

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[5] [illegible], Ber. [illegible]

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THE PROBLEM OF METALLOORGANIC COMPOUND FORMATION BY INTERACTION OF AN AROMATIC SILANE WITH METAL CHLORIDES

III. FORMATION OF THE ORGANOANTIMONY COMPOUND BY INTERACTION OF PHENYL CHLOROSILANE WITH $SbCl_5$

A. Ya. Yakubovich and G. V. Motsarev

It was mentioned earlier that the interaction of phenylchlorosilanes with $AlCl_3$ [1], and in some cases with $FeCl_3$ [2], is accompanied by rupture of the Si–C bond, with simultaneous formation of the aromatic aluminum-, and, evidently, unstable organoiron compounds. It was of interest, therefore, to explain the relationship of phenylchlorosilanes to the chlorides of antimony ($SbCl_3$ and $SbCl_5$), whose interactions have not hitherto been investigated.

Experiments have indicated that in contrast to $AlCl_3$, and $FeCl_3$, $SbCl_3$ is not found to be a dearylating agent. In actuality, if, for example, diphenyldichlorosilane ruptures $AlCl_3$ or $FeCl_3$ at 30°, then $SbCl_3$ will not react with it, even at 200°.

However, in the case of $SbCl_5$, it was found that rupture of diphenyldichlorosilane proceeds very readily at normal temperature. Upon mixing diphenyldichlorosilane, both in molar ratio and with excess $SbCl_5$ (2 moles), intense reaction is observed, accompanied by heat evolution and appearance of orange coloration. The products of this reaction were found to be phenyltrichlorosilane, chlorobenzene and $SbCl_3$. This indicated that $SbCl_5$ reacts with a molecule of diphenyldichlorosilane with rupture of the Si–C bond only, independently of the presence of $SbCl_5$ excess. The latter was also confirmed by special experiments on the study of the interaction of phenyltrichlorosilane with $SbCl_5$, which have demonstrated that reaction between them does not occur, even with heating.

Analogous results were observed for the reaction of $SbCl_5$ with di-(p-chlorophenyl)-dichlorosilane, and also as obtained by organomagnesium synthesis:

$$2p\text{-}C_6H_4ClMgBr + SiCl_4 \rightarrow (p\text{-}C_6H_4Cl)_2SiCl_2 + 2MgBrCl$$

at normal temperature. From the reaction products in this case were obtained p-chlorophenyltirchlorosilane (identified by the corresponding resin), p-dichlorobenzene and $SbCl_3$.

A comparison of the results obtained made it possible to assume that rupture of diphenyldichlorisilane and its halogen derivatives by antimony pentachloride proceeds according to Equation (1), with formation of an intermediate, unstable under normal conditions, organoantimony compound, readily decomposed at the C–Sb bond according to Equation (2) (Ar = Aromatic radical).

$$Ar_2SiCl_2 + SbCl_5 \rightarrow ArSiCl_3 + ArSbCl_4; \qquad (1)$$

$$ArSbCl_4 \rightarrow ArCl + SbCl_3. \qquad (2)$$

This assumption was successfully proved by experiment.

If rupture is carried out at lowered temperature (−20°), then formation, for example, of phenylstibintetrachloride, resulting from such procedure, can be easily proved by conversion to phenylstibinic acid, which was isolated in a yield of 55% of theory.

$$(C_6H_5)_2SiCl_2 + SbCl_5 \rightarrow C_6H_5SiCl_3 + C_6H_5SbCl_4 \xrightarrow{+3H_2O} C_6H_5SbO(OH)_2 + 4HCl \qquad (3)$$

Consequently, the described interaction of aromatic silanes with $SbCl_5$ proceeding readily under the conditions described is found to be a new synthetic method for aromatic stibines.

Thus, the accuracy of the proposed rupture mechanism of diphenyldichlorosilane and its derivatives of $SbCl_5$ under normal conditions, as indicated in Equations (1) and (2), is confirmed not only by the possibility of isolating the corresponding silicon-containing rupture products of phenylchlorosilane, but also by the proved formation of intermediate organoantimony compounds.

It is indeed obvious that the interaction of phenylchlorosilanes and their derivatives with $SbCl_5$ proceeds according to a mechanism similar to the interaction mechanisms of phenylchlorosilanes with $AlCl_3$ and $FeCl_3$. Actually, in the case of all three of these chlorides, the rupture of aromatic silanes by them proceeds very easily, and the reaction products are found to be on the one hand silicon-containing compounds ($SiCl_4$ and $C_6H_5SiCl_3$), and on the other, organic compounds of aluminum, antimony or iron.

According to their dearylating activity, the indicated chlorides can be arranged in the following decreasing order $AlCl_3 > FeCl_3 > SbCl_5$, according to which there is observed this or some other degree of ease of rupture at the C–Si bond of aromatic silanes.

EXPERIMENTAL

Interaction of Diphenyldichlorosilane with $SbCl_3$

5.25 g (0.023 mole) of antimony trichloride, purified beforehand by vacuum distillation, was added to 5 g (0.02 mole) of diphenyldichlorosilane. The mixture was heated for 7 hours at 150-200°, after which the reaction products were distilled in vacuo. The resulting fractions were: 1) b.p. 80-90° at 6 mm – 5.0 g; 2) b.p. 90-135° at 6 mm – 0.3 g; 3) b.p. 135-145° at 6 mm – 4.3 g. There remained in the residue 0.5 g of dark resin.

Upon standing, the first fraction crystallized; upon repeated distillation, 4.6 g of antimony trichloride was isolated. The antimony found was 53.0%, theory 53.3%. Upon repeated distillation of the 3rd fraction, 4.0 g of colorless liquid resulted, with a sharp odor, and b.p. 142-144° at 6 mm, representing unchanged diphenyldichlorosilane.

Found %: Cl 27.8; Si 11.0. $C_{12}H_{10}SiCl_2$. Calculated %: Cl 28.0; Si 11.07.

Interaction of p,p'-Dichlorodiphenyldichlorosilane with $SbCl_5$

6.0 g (0.02 mole) of antimony pentachloride was added gradually to 5.0 g (0.021 mole) of p,p'-dichlorodiphenyldichlorosilane. Upon mixing the reactants, a strong heat evolution (up to 80°) was observed in the reaction mass, with a color change to orange. After addition of the total amount of antimony pentachloride, the mixture was heated for 5 hours at 80-90°. The reaction product was distilled in vacuo, wherein a fraction with b.p. 70-105° at 13 mm was isolated in the amount of 7.5 g, which, upon standing, crystallized partially. The crystals which separated from the liquid portion upon cooling to 0° were found to be antimony trichloride (3.0 g). The liquid portion was treated with water and distilled with steam. The water distillate contained crystals which, after separation from water, and recrystallization from petroleum ether, had a m.p. of 53°, and were p-dichlorobenzene.

Found %: Cl 48.1. $C_6H_4Cl_2$. Calculated %: Cl 48.3. Yield 1.8 g, 78% of theory.

The residue in the distilling flask was a transparent resin, which from its chlorine and silicon contents, corresponded to the resin isolated from monochlorophenyltrichlorosilane.

0.1210, 0.1276 g substance: 0.1078, 0.1131 g AgCl (Carius). 0.2001, 0.2090 g substance: 0.0723, 0.0759 g SiO_2. Found %: Cl 22.1, 22.0; Si 16.9, 17.0 $(C_6H_4ClSiO_{1.5})_n$. Calculated %: Cl 21.7; Si 17.1

From the quantity of reaction products isolated, it follows that rupture of p,p'-dichlorodiphenyldichlorosilane by antimony pentachloride under the conditions given, proceeded on the average to 80% completion.

Interaction of Diphenyldichlorosilane with $SbCl_5$

a) At a decreased temperature (–20°). Synthesis of phenylstibinic acid. 5.9 g (0.0196 mole) of antimony pentachloride, precooled to –20°, was gradually added to 5.0 g (0.0197 mole) of diphenyldichlorosilane, also precooled to –20°. The reaction mass, at first dark-green in color, rapidly changed to dark-orange.

The mixture was twice treated with concentrated hydrochloric acid saturated with hydrogen chloride, with cooling, to remove antimony trichloride, the formation of which was to be expected because of partial rupture of phenylstibinetetrachloride The hydrochloride solution, upon dilution with water, produced a white precipitate of antimony oxide, soluble in concentrated hydrochloric acid.

Subsequent treatment of the mixture with water, and cooling, led to formation of a copious precipitate, white in color, and a viscous tar, which was extracted with ether. The ether layer was separated, and the ether distilled off. After distilling off the ether, 2.0 g (78.4% of theory) resulted of the resin, which corresponded in analysis of silicon content to the resin which resulted from phenyltrichlorosilane. The silicon found was 20.9%, in theory 21.7.

The white-colored precipitate contained in the water layer (after separation of the ether layer) was filtered off, washed several times with ether, then with water, and dried. From an analysis of the antimony content (found 50.1%; theory, 49.83%), and from the properties (an amorphous powder, insoluble in water, soluble in aqueous ammonia, soda, alkaline hydroxide and in glacial acetic acid), the substance corresponded to phenylstibinic acid. 2.7 g, or 55% of theory, resulted.

b) At normal temperature. 23.6 g (0.079 mole) of antimony pentachloride was gradually added to 10.0 g (0.039 mole) diphenyldichlorosilane. There occurred a strong heat evolution in the mixture, and formation of a dark-orange color. After suitable treatment (see preceding experiment), 15.5 g of antimony trichloride and 3.6 g of a liquid with b.p. 130-131° resulted, identified from its boiling point and density (d_4^{20} 1.1069) as chlorobenzene. The chlorine found was 31.1%, theory 31.5. The yield of chlorobenzene was 81.4% of theory.

The residue in the distilling flask after distilling with steam was a transparent resin, which, by analysis, of the silicon content, corresponded to the resin which resulted from phenyltrichlorosilane. The silicon found was 21.3%, theory 21.7%.

SUMMARY

1. The interaction of antimony trichloride and of pentachloride with phenyltrichlorosilane, diphenyldichlorosilane and its p,p'-dichloroderivative have been studied

It has been found that in contrast to the primary chlorosilanes, the secondary are very easily ruptured by antimony pentachloride, in such a manner that the primary aryltrichlorosilane is formed, the antimony trichloride splitting the aryl radical from it, thus transforming to the corresponding chloroderivatives.

2. It has been proved that the mechanism of the above-indicated interaction of aryldichlorosilanes with antimony pentachloride consists of a disproportionation reaction between them, which is accompanied by the formation of an unstable arylstibinetetrachloride, which decomposes under normal conditions into antimony trichloride and the arylchloride

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* See Consultants Bureau Translation, page 805.
** " " " " " 1111.

INVESTIGATION OF THE ALKALOIDS OF SENECIO SPECIES

VIII. ALKALOIDS FROM THE SPIRAL RAGWEED (SENECIO SARRACENIUS)

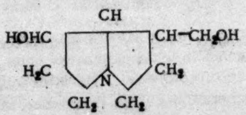
A. Danilova, R. Konovalova, P. Massagetov and M. Garina

In the author's laboratory, investigations have been carried out chiefly upon various species of ragweed growing in the Caucasus and in Middle Asia. A study of the alkaloids isolated from various species of ragweed [1] is without doubt of theoretical and practical import. Suffice to point out that platiphyllin [2] from the broadleaf ragweed is used in medical practice as a spasmolitic and as an agent for decreasing blood pressure. It was, therefore, of interest to study various species of ragweed growing in other regions of the Soviet Union. In 1949, the VNIKhFI* expedition, under the leadership of P. S. Massagetov, collected in the Altai the above-ground portions of spiral ragweed (Senecio sarracenius) during the blossoming phase. The plant was collected on the banks of the River Bukhtarma in August. This perennial grassy plant is wide-spread in the area of water basins. It occurs in Western Europe, the European section of the USSR, and in Siberia.

The spiral ragweed contains considerable quantities of alkaloids, from 0.8 to 0.9%. Isolation of the alkaloids was carried out by the usual method, namely, by extracting the plant with dichloroethane, moistened beforehand with ammonia, and by extracting the bases from the alkaline solution, first with ether, and then with chloroform. A mixture of alkaloids resulted from the ether solution in the form of a viscous mass. The crystalline bitartrate of a base, having an m.p. of 177-179°, was obtained from the mixture using an alcoholic solution of tartaric acid. An anhydrous base was obtained from the bitartrate in the form of a colorless liquid, turning yellow rapidly in the light. Upon mixing with several drops of water, the base converted to a powder. After recrystallizing from water, m.p. 51-52°, $[\alpha]_D -129.7°$. The composition of the anhydrous base was $C_{18}H_{27}O_5N$. In composition, the base isolated was isomeric with platiphyllin, but not identical with it. From its properties, and also from the properties of the salts, the alkaloid isolated differed from the bases described, and was named "sarracin" by the authors. Sarracin is readily soluble in alcohol, ether, chloroform, poorly so in water, forming a crystalline picrate, m.p. 140-141°. It contains an hydroxyl group, and does not contain the methylimidine group. It decolorizes readily a solution of potassium permanganate. As with other alkaloids isolated from various ragweed species, sarracin has the properties of an ester. Upon heating with alkali, it decomposes into an aminoalcohol and organic acids.

The aminoalcohol is a crystalline compound with m.p. 151-152° and $[\alpha]_D -57°$ (c = 1.4 in $CHCl_3$). It decomposes readily in water, alcohol, is poorly soluble in chloroform, and is almost insoluble in ether and petroleum ether. It forms a picrate with m.p. 184-185°. The properties of the aminoalcohol and of its salts coincide exactly with the properties of platinecine, which was obtained by R. A. Konovalova and A. P. Orekhov by hydrolysis of platiphyllin. By direct comparison of both bases, the authors have established their exact identity.

As the result, the aminoalcohol resulting from hydrolysis of sarracin has been found to be platinecine [3], for which the following structure has been established:



The unsaturated properties of sarracin are explainable by the presence of a double bond in the esterifying acids. Thus, sarracin differs from platiphyllin by the nature of the esterifying acids.

Considering the fact that the alkaloids separated from various ragweed species, and the closely-related alkaloids from heliotropium, are frequently found in plants as the N-oxide form, it can be assumed that N-oxides of the alkaloids in spiral ragweed are also present. In fact, by extracting the alkaloids from the plant by chloroform, without ammonia pre-moistening, the authors isolated a substance which possessed an almost neutral character, whereas alkaloids possessing basic properties that were present as salts in the plant were not extractable by chloroform. In this way, a second alkaloid of the composition $C_{18}H_{27}O_6N$ was isolated, containing one more oxygen than sarracin. This new alkaloid, after recrystallization from acetone, had an m.p. of 123-124° and $[\alpha]_D$ −81.65°. It dissolved readily in water and alcohol, and with great difficulty in ether. It formed a crystalline picrate with m.p. 107.5-108.5°, and a chloroaurate with m.p. 153-155°. Upon reduction with zinc dust in hydrochloric acid medium, it converted to sarracin.

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All of the indicated properties of the newly isolated alkaloid permitted the assumption that an oxygen atom is directly connected with nitrogen in the molecule, and is therefore the N-oxide of sarracin. To confirm the accuracy of this assumption, the N-oxide of sarracin was synthesized by reacting sarracin with hydrogen peroxide. A direct comparison of the substance resulting by this procedure with the N-oxide of sarracin demonstrated their complete identity.

The authors found by further work that total alkaloid extraction from spiral ragweed is more convenient with isopropyl alcohol acidified with acetic acid. Under these conditions, isopropyl alcohol also extracts the N-oxide form of sarracin as well as sarracin itself. Reduction of the total isolated bases with zinc dust in hydrochloric acid medium gave sarracin in an amount sufficient for additional study.

EXPERIMENTAL

Isolation of the Alkaloids. Dry, finely powdered plant, in the amount of 17 kg, was exhaustively extracted with isopropyl alcohol, to which was added acetic acid (2% to the volume of alcohol). The alcohol was distilled off in vacuo to a residue of thick consistency. The latter was dissolved in benzene. The benzene solution was extracted several times with 10% sulfuric acid The acid solutions were combined, filtered, washed in a separatory funnel, first with benzene and then with ether. The hydrochloride solution of alkaloids was alkalized with 25% ammonia, with cooling, to an alkaline reaction for phenolphthalein, and extracted with ether. By this procedure a considerable portion of the sarracin (I) converted to the ester.

The aqueous solution was then extracted with ether, acidified with sulfuric acid to an acid Congo reaction, and reduced with zinc dust, using mechanical stirring. The acid solution resulting from reduction of the N-oxide was alkalized with ammonia and extracted, first with ether (II) and then with chloroform (III). The ether solutions (I) and (II) were combined and dried over Na_2SO_4. After distilling off the ether, 147 g of alkaloids resulted in the form of a light-brown colored viscous mass.

The chloroform solution (III) was dried over Na_2SO_4. After distilling off the chloroform, 18 g of dark-brown colored resinous bases resulted. It was not possible to obtained any characteristic salts.

Synthesis of the Sarracin Salts. The 147 g of alkaloids obtained after distilling off the ether were dissolved in 120 ml of alcohol, and to the alcoholic solution was added 80 g of tartaric acid dissolved in 200 ml of alcohol. The mixture was heated to boiling on a reflux. The resulting sarracin bitartrate was filtered off with suction and washed with alcohol. After three crystallizations from alcohol, 1:10, 40 g of sarracin bitartrate resulted with m.p. 177-179°. An additional 10 g of sarracin bitartrate was isolated from the mother liquors.

0.2455 g substance: in 4.5 ml water; α_D −1.91°, $[\alpha]_D$ −70.05°; $\underline{1}$ 0.5 dm. 3.796 mg substance: 7.556 mg CO_2; 2.315 mg H_2O. 4.499 mg substance: 8.884 mg CO_2; 2.716 mg H_2O. 8.295 mg substance: 0.218 ml N_2 (26.0°, 732.0 mm). 9.215 mg substance: 0.239 ml N_2 (22.0°, 734.0 mm). Found %: C 54.29, 53.89; H 6.82, 6.75; N 2.89, 2.91. $C_{18}H_{27}O_5N \cdot C_4H_6O_6$. Calculated %: C 54.20; H 6.77; N 2.87.

Isolation of Sarracin Base from the Bitartrate. 10 g of sarracin bitartrate was dissolved in 50 ml of water. The aqueous solution was alkalized with 25% ammonia in the presence of ether. The sarracin base which separated out in the form of colorless oily drops readily dissolved in ether. The ether solution was filtered. 6.5 g of sarracin resulted after distilling off the ether. After recrystallizing twice from water, sarracin resulted with m.p. 50-52°.*

0.4450 g substance. in 4.5 ml alcohol; α_D −12.83°; $[\alpha]_D$ −129.7°; $\underline{1}$ 1 dm. 4.890 mg substance: 11.507 mg CO_2; 3.581 mg H_2O. . 8.900 mg substance; 0.327 ml N_2 (21.0°, 738.5 mm). 14.260 mg substance: 0.531 ml N_2 (26.5°, 730.0 mm). 5.971 mg substance: 0.47 ml CH_4 (26.0°, 751.0 mm). 5.144 mg substance: 0.39 ml CH_4 (26°, 748.0 mm). Found %: C 64.17; H 8.19; N 4.15, 4.07; OH 5.50, 5.30. $C_{18}H_{27}O_5N$.

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* For analysis the compound was taken on the basis of water of crystallization.

Calculated %: C 64.09; H 8.01; N 4.15; OH 5.04.

Sarracin Picrate. 2.8 g of sarracin base was dissolved in 15 ml of alcohol. Picric acid was added to the saturated alcoholic solution. The sarracin picrate which separated out was filtered with suction and washed with alcohol. After 2 recrystallizations, from alcohol (1: 3), the m.p. of the picrate was 140-141°.

2.855 mg substance: 5.339 mg CO_2; 1.379 mg H_2O. 4.785 mg substance: 0.418 ml N_2 (24.5°, 736.0 mm). Found %: C 51.03; H 5.39; N 9.92. $C_{18}H_{27}O_5N \cdot C_6H_3O_7N_3$. Calculated %: C 50.88; H 5.30; N 9.87.

Extraction of Sarracin N-oxide from the Plant. The alkaloids were exhaustively extracted by chloroform from 700 g of pulverized plant. The chloroform extracts were combined and extracted with 10% sulfuric acid. The acid solution was filtered off and alkalized with ammonia, with cooling. The alkaloids from the alkaline solution were extracted with chloroform. The chloroform extract was dried over anhydrous sodium sulfate. After distilling off the chloroform, 1.8 g of alkaloids resulted, which constituted 0.25% of the total plant weight taken. After 3 recrystallizations from acetone, the m.p. of the sarracin N-oxide was 123-124°. The oxide was readily soluble in water and alcohol and poorly so in ether and acetone.

0.4542 g substance in 4.5 ml water, $\alpha_D -4.12°$, $[\alpha]_D -81.65°$; $\underset{\rightarrow}{1}$ 0.5 dm, 5.395 mg substance: 0.196 ml N_2 (23.5°, 731.0 mm). Found %: N 4.02. $C_{18}H_{27}O_6N$. Calculated %: N 3.96.

Sarracin N-Oxide Picrate. Sarracin N-oxide in the amount of 1.5 g was dissolved in 5 ml of alcohol. A saturated alcoholic solution of picric acid was added to the solution. The picrate separated out as a precipitate upon rubbing with a glass rod. After recrystalizing three times from alcohol, m.p. was 107.5-108.5°.

2.990 mg substance: 5.364 mg CO_2; 1.424 mg H_2O. 0.355 mg substance: 0.378 ml N_2 (22.0°, 736.0 mm) 4.845 mg substance: 0.423 ml N_2 (26.5°, 740.00 mm). Found %: C 48.96; H 5.33; N 9.73, 9.69. $C_{18}H_{27}O_6N \cdot C_6H_3O_7N_3$. Calculated %: C 49.48; H 5.15; N 9.62.

The Chloroaurate of Sarracin N-Oxide. Sarracin N-oxide in the amount of 0.2 g was dissolved in 5 ml of 10% hydrochloric acid, to which was added an aqueous solution of $HAuCl_4$. The resulting chloroaurate precipitate was filtered off with suction and washed with hydrochloric acid. After one recrystallization from acidified water, the m.p. was 153-155°. The chloroaurate of the N-oxide is an unstable salt. With heating and upon long standing in the light, it decomposes readily.

3.626 mg substance: 1.059 mg Au. 5.555 mg substance: 1.607 mg Au. Found %: Au 29.20, 28.93. $C_{18}H_{27}O_6N \cdot HAuCl_4$. Calculated %: Au 28.45.

Reduction of Sarracin N-Oxide with Zinc Dust. Sarracin N-Oxide in the amount of 0.5 g was dissolved in 10 ml of 10% sulfuric acid. 2 g of zinc dust was gradually added to the solution with stirring. The resulting solution was filtered, alkalized with ammonia and extracted with ether. After distilling off the ether, 0.3 g of sarracin resulted with m.p. 41-42°. Due to difficulty in purifying and identifying sarracin as the base, the bitartrate was obtained. The latter, after recrystallization from alcohol, melted at 177-178°, and did not give depression in melting point with sarracin bitartrate isolated from the plant.

Oxidation of Sarracin with a 3% Solution of Hydrogen Peroxide. 12 ml of 3% hydrogen peroxide was added to 1.3 g of sarracin base. The mixture was left at room temperature for 48 hours. After lapse of the indicated time, all of the substance went into solution. The acid aqueous solution was alkalized with ammonia, with cooling, and extracted with ether. Non-oxidized sarracin went into the ether. After extraction with ether, the aqueous solution was extracted with chloroform. The chloroform solution was dried over anhydrous sodium sulfate. After distilling off the chloroform, 0.38 g of substance, with m.p. 122-123°, was obtained, which did not give depression in melting point with sarracin N-oxide isolated directly from the plant.

Hydrolytic Rupture of Sarracin. 50 ml of 0.5 N alcoholic potassium hydroxide solution was added to 4.3 g of sarracin, and the mixture boiled over reflux for 3 hours. The alcohol was distilled off to dryness. The residue was acidified with 10% sulfuric acid and extracted with ether. The ether solution was dried over anhydrous sodium sulfate. After distilling off the ether, 2.5 g of viscous non-crystalline acid was obtained. The acid aqueous solution which remained after extraction with ether was alkalized with 25% alkali, and was then extracted first with ether and then with chloroform. The ether and chloroform solutions were dried over anhydrous sodium sulfate.

After distilling off the ether, 0.5 g of the liquid aminoalcohol resulted, which formed a crystalline picrate, m.p. 264-266°, with an alcoholic solution of picric acid. The properties of the liquid aminoalcohol and its picrate coincided with the properties of anhydroplatinecin and the picrate of the latter. There was no depression upon determining the melting point of a mixture of the liquid aminoalcohol picrate from the spiral ragweed with anhydroplatinecin picrate. After distilling off the chloroform, 1.2 g of crystalline aminoalcohol resulted with m.p. 146-149°. After 2 recrystallizations from acetone, m.p. 151-152°. Readily soluble in water and alcohol, poorly so in acetone and ether, almost insoluble in petroleum ether. With an alcoholic solution of picric acid, it formed a crystalline picrate with m.p. 184-185°.

The specific rotation of the aminoalcohol was $[\alpha]_D - 85.16°$ (c = 1.22, in alcohol): $[\alpha]_D - 57°$ (c = 1.4, in $CHCl_3$.

No depression was observed in determining the melting point of a mixture of the aminoalcohol from spiral ragweed with platinecin obtained by saponification of platiphyllin, nor for a mixture of their picrates.

Analyses were carried out in the microanalytical laboratory of VNIKhFI under the supervision of V. V. Kolpakova.

SUMMARY

1. Two new alkaloids, sarracin $C_{18}H_{27}O_5N$, and sarracin N-oxide, $C_{18}H_{27}O_6N$, have been isolated from the spiral ragweed (Senecio sarracenius).

2. It has been determined that sarracin represents an ester of platinecin and organic acids.

3. Sarracin picrate and bitartrate have been obtained, as well as the picrate and chloroaurate of sarracin N-oxide.

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* See Consultants Bureau Translation, page 1989.

SPECTROGRAPHIC INVESTIGATION OF CARDIAC GLYCOSIDES FROM HELLEBORE

M. Ya. Tropp, Yu. V. Shostenko and D. G. Kolesnikov*

The cardiac glycosides represent a group of rather valuable medicinal substances. Because of the complexity in structure, the ease of rupture, and the isomerizability of cardiac glycoside molecules, and also since they occur in very small amounts in plants, their chemical study, represented by a series of works (see reviews [1, 2]) is still far from complete.

The purpose of the present work was to utilize absorption spectra in the ultra violet for investigation of new cardiac glycosides, and to attempt their utilization for analytical determination of the latter. As the objects of investigation, new crystalline glycosides from the phyto-chemical laboratory of the Kharkov Scientific Research Chemico-Pharmaceutical Institute were taken by Kolesnikov and Tropp [3], from the roots of the caucasian (Helloborus caucasicus A. Br.) and the red (Helleborus purpurascens W. and K.) hellebores. The first of them was named corelborin K, and the second, corelborin P. A study of the two glycosides by the authors indicated [3], gave some grounds for belief that the two glycosides belong to glycosides of the scillarene group, isolated for the first time from a domestic raw material.

EXPERIMENTAL

Investigation of the absorption spectra for the cardiac glycosides, and their transformation products, was carried out with the help of a quartz spectrograph ISP-22. An arc between the electrodes and tungsten steel served as the light source. The glucose solution was placed in a cell with variable absorption layer thickness. The solvents used were — water and ethyl alcohol — purified in an appropriate manner, and their optical transparency verified by spectrographic means in the 2200-4000 A range. The original glycosides were pure, crystalline substances, of constant melting points.

To obtain the absorption curves, the authors took spectrograms based upon a minimal exposure time for the solvent [4]. Solutions of the substances investigated and the solvent were successively photographed at absorption layer thicknesses of 0.5, 1, 2, 2.5 and 5 cm. Exposure for the solvents was 10 seconds, and for the solutions, from 40 to 100 seconds.

X-ray film (with a sensitivity of 250, H and D) was used, which was placed in the spectrograph frame by a special holder to avoid bending. The photometry was carried out visually by means of a magnifying glass. For convenience in visual photometry, it is necessary that the solvent spectrum be situated in the photograph exactly beneath the solution spectrum (without any break between them). To meet this requirement, the authors prepared a special diaphragm with two horizontal openings, one shifted in relation to the other, and arranged in such a manner that the upper limit of one aperture went into the lower limit of the other.

The length of each aperture was 0.8 mm. The use of such an aperture ensured the obtaining of spectral pairs closely aligned to each other.

To eliminate possible errors, photographing of the absorption spectra was carried out from one direction by shifting the frame. In addition, to verify reproducibility of results, the same absorption curve was photographed and photometered several times. The concentration of solution investigated was 10^{-4} or 10^{-5} moles/liter.

EVALUATION OF RESULTS

Absorption curves for corelborin P and corelborin K in ethanol are given in Fig. 1. These curves have a characteristic maximum at 3000 A, and a minimum at about 2475 A. A similar maximum is also found for the absorption curves of hellebrin and desglucohellebrin glycosides from the black hellebore which were isolated and studied by Karrer and Schmut [5]. These circumstances, together with the results of other experiments [3], have given the basis, as has already been indicated, for referring both glycosides to that group of glycosides which possesses a six-membered unsaturated lactone ring with 3 conjugated double bonds, inasmuch as the glycosides of a five-membered lactone ring (two conjugated double bonds), according to both the literature [2] and the authors' data, (Fig. 1), have a characteristic maximum in the range 2200 - 2300 A.

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* S. Yanova participated in the experimental part of the work.

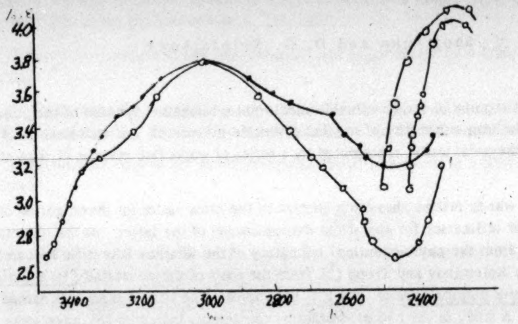


Fig. 1. Absorption Curves.
1) Corelborin K; 2) corelborin P; 3) convallatoxin; 4) convalloside.

The close similarity of the two curves presented in Fig. 1 speak for the close resemblance in structure of the two glycosides from hellebore; at the same time, however, they differ so much from each other (minimum position at 2475 A) that there is no doubt about the fact that they belong to two different substances. The higher value, log ϵ, in the range of 2350 - 2750 A for corelborin P is apparently related to the presence of an additional sugar molecule in the molecule (as compared to corelborin K), which increases the intensity of absorption in this range at the expense of additivity in absorption. In the same Fig. 1 absorption curves are given for two other individual glycosides of domestic manufacture, as isolated by the authors — convallatoxin and convalloside, differing from corelborin K and corelborin P only in the respect that they possess a five-membered lactone ring instead of a six-membered lactone ring. In this case, also in the range 2340 - 2500 A, the convalloside absorption curve which contains one more sugar molecule than convallatoxin lies above the curve of the latter.

A comparison of the Fig. 1 curves shows clearly the extent to which the absorption spectra of cardiac glycosides depend upon the structure of the lactone ring. The introduction of one additional conjugated double bond shifts sharply the entire absorption curve into the long wave length region. This fact makes it possible to utilize absorption spectra as the principal and most reliable indication for classification of cardiac glycosides into a group containing the five-membered unsaturated lactone ring, and a group containing the six-membered ring, along with the sodium nitroprusside color reaction (in 1N NaOH), the sodium picrate (in neutral medium), and with acetic anhydride and sulfuric acid. It should be noted at the same time that it follows from the authors' and the literature data [2] that the absorption spectra of cardiac glycosides (or their aglucones) differ only by substituents in the ring (for the same sugars and same lactone ring), differing little from one another, and therefore cannot serve practically for identification of individual substances.

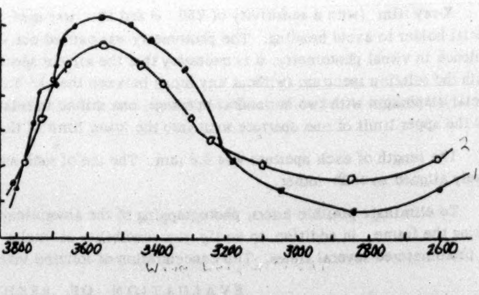


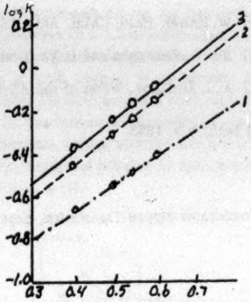
Fig. 2. Absorption Curves for Lactone Titration Products.
1) Corelborin K; 2) corelborin P.

Cardiac glycoside molecules hydrolyze readily. In an acid medium this leads to splitting of the sugar component, but in an alkaline medium, however, depending upon conditions, leads to rupture of the lactone ring, or to more extensive changes in the molecule. It was of interest to follow by means of absorption spectra the hydrolysis of corelborin

K and corelborin P in alkaline medium. For this purpose, both glycosides were subjected to so-called lactone titration in 75% ethanol, i.e., they were treated with 0.1 N NaOH for 48 hours, and the alkali excess then titrated with 0.1 N HCl. In Fig. 2 absorption curves are presented for lactone titration products of both glycosides. Quite evident is the increase of absorption intensity and displacement of the maximum at 3000 A to 3550 A. It should be mentioned that the absorption spectrum for an alkaline solution of corelborin K (before acidification) had an analogous maximum. Similar change in absorption spectra speaks for the fact that under the influence of alcoholic alkali, for the conditions indicated, non-reversible transformation of the unsaturated six-membered lactone ring evidently takes place. This was confirmed by biological tests of the lactone titration product, which was found to be biologically inactive.*

A similar phenomenon was also observed upon polarographic investigation of strophantidine [6], where the action of a 0.03 N-solution of $(CH_3)_4NOH$ did not lead to an irreversible formation of non-reducible isoform of strophantidine at the dropping-mercury alectrode, but the action of 0.1 N-solution led to formation of the isoform in 15 hours, which, upon acidification, did not change to the original compound. It is characteristic that the absorption curve for the alkaline reaction product of strophantidine (following acidification of the solution) was shifted relative to the strophantidine curve itself toward the long waves, as with corelborin K and corelborin P.

The chief method for quantitative determination of cardiac glycosides up to the present time has been the biological method. This is more with respect to glycosides possessing the six-membered lactone ring, since more or less satisfactory colorimetric methods are available [7] for glycosides with the five-membered ring. In this regard the authors decided to use the absorption spectra for quantitative determination of corelborin K. Inasmuch as it is liberated as a solution in 0.4% chloroethone solution, it was determined that a 0.4% solution of chloroethone** is optically transparent in the spectral range of interest as the result of which qualitative determination of glycoside is possible directly in this solution.



Concentration (in mg/10 ml).

Fig. 3. Standard curves for quantitative determination of corelborin K. 1) 3200 A; 2) 3100 A; 3) 3000 A.

As the result of photographic recording of absorption curves for a number of corelborin K solutions of known concentrations in 0.4% chloroethone, several standard straight lines (for various λ) (Fig. 3) were obtained. For quantitative determination, the straight line 3 was chosen (at 3000 A), corresponding to that wave length where change in Δ log K/Δλ is small, inasmuch as the probability of experimental error in measurement for constructing the absorption curves is smallest in this range. By means of this straight line a quantitative determination of corelborin K was carried out in a solution of known concentration (see Table).

Quantitative Analysis of an Ampoulated Solution of Corelborin K

Quantity of substance taken (for 10 ml of solution, in mg)	Wave lengths								
	3000 A			3100 A			3200 A		
	Found	Difference	Error (%)	Found	Difference	Error (%)	Found	Difference	Error (%)
0.595	0.600	0.005	0.84	0.600	0.005	0.84	0.560	−0.045	−7.60
0.475	0.460	−0.015	−3.20	0.425	−0.050	−10.5	0.400	0.075	−15.80
0.370	0.380	0.01	2.70	0.365	−0.005	−1.40	0.400	0.030	8.10

Thus, for more accurate analysis, the absorption spectra should be taken at 0.02 unit intervals on the log K scale. At the same time, while carrying out serial analyses, there is no need to take all of the curve, for it can be limited to that section selected for the calculated wave length range.

SUMMARY

1. Absorption curves for the new cardiac glycosides containing the six-membered lactone ring, isolated from domestic material, have been obtained.

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* Glycosides with a ruptured lactone ring are usually found to be biologically inactive.

** "Chloroethone" = $C_4H_7OCl_3 \cdot \frac{1}{2} H_2O$ (acetone-chloroform) and is added as a preservative to the ampoulated solutions.

2. It has been found upon prolonged action of alkaline solution on corelborin K and corelborin P, that they undergo irreversible transformation into biologically-inactive products which possess absorption spectra differing sharply from the glycoside spectra themselves. This phenomenon can be used to detect glycoside transformation products in mixture with glycosides, and qualitative reactions also give a positive result.

3. Quantitative determination of corelborin K in ampoulated solutions has been carried out by the use of absorption spectra.

4. The difference between absorption spectra for cardiac glycosides of the digitalic -strophantic and scillarene groups can be used as a reliable method for determining to which of two groups cardiac glycosides belong.

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* See Consultants Bureau Translation, page 155.

A STUDY ON FURANE COMPOUNDS

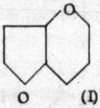
III. THE STRUCTURE OF 1,6-DIOXASPIRO-(4,4)-NONANES AND THEIR FORMATION MECHANISM

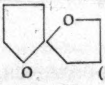
A. A. Ponomarev, V. A. Afanasyev and N. I. Kurochkin

It has been mentioned earlier [1] that hydrogenation of furane aldehydes and ketones is accompanied by the formation of bicyclic, non-hydroxylated compounds, along with the corresponding alcohols.

The problem of the structure for these compounds has already been investigated in the special literature.

Adkins and Burdick [2], having discovered for the first time similar compounds among the hydrogenation products of furylacrolein by the use of Raney nickel (NiR), assumed the presence of a 1,5-dioxaoctahydrindene structure, i.e., Formula (I), based upon the absence of characteristic acetal reactions for this compound. In their following work [3], these authors indicated a change in their point of view, because of the identity of this product with the compound obtained at the end of the last century by Fittig [4] from butyrolactone, and which was named by him oxetone, from the latter of which, by the action of HI was formed diiodopropylketone and from the latter dipropyl ketone was formed by reduction, which is in complete accord with the properties that Fittig found for his compound. All of this has led to the thought that the compound forming by hydrogenation of furylacrolein in actuality has the spirane structure corresponding to Formula (II):


(I)


(II)

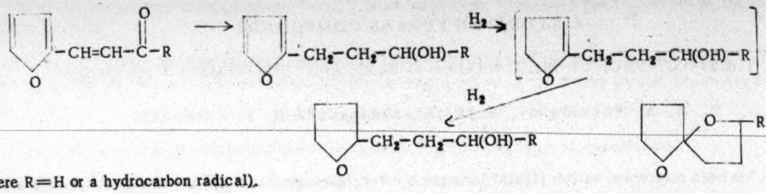
Later, the product was obtained in better yield by hydrogenation of furylpropanol in the presence of nickel on kieselguhr [5].

The structure for the nearest homolog of this spirane — 2-methyl-1,6-dioxaspiro-(4,4)-nonane — which is formed by hydrogenation of furfurylideneactone over NiR [6], or of furylbutanol over Ni on kieselguhr [5], was confirmed as in the preceding case by its conversion upon heating with HI into diiodoketone, and by reduction of the latter to octanone-4 [5].

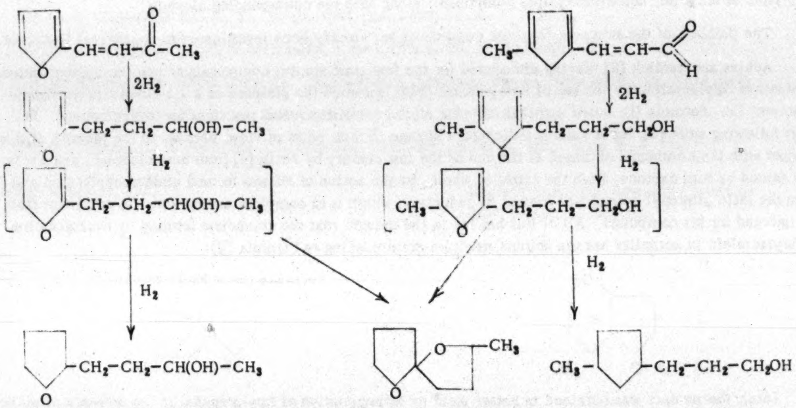
There has also appeared information in the literature on the formation of the analogous bicyclic products from hydrogenation of difurfurylideneacetone [7], α-ethyl-β-(α-furyl)acrolein [6] and α-methyl-β-(α-furyl)acrolein [8]. However, in the latter instances, the authors have not sufficiently substantiated the structures of the products obtained. Furthermore, Hinz, Meyer and Schucking [6] in their article on the formation of bicyclic products by hydrogenation of furylacrolein, furfurylideneacetone and α-ethyl-β-(α-furyl)acrolein, again attribute to them the structure of the cyclic dioxaoctahydrindene.

Though the analytical proofs given earlier [3, 5] for the simplest spirane structure, and its methyl homolog, are sufficiently convincing, nevertheless it should be mentioned that a new synthetic proof for 1,6-dioxaspironbackslash-onanes can be predicted, based upon the hydrogenation of certain furane aldehydes and ketones. This is possible on the basis of silvane hydration, which is similar to hydrogenation and which is similar to the concept of the spirane formation mechanism: (see next page)

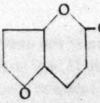
It is not difficult to see that in the case of a similar reaction mechanism, hydrogenation of two compounds — furfurylideneacetone and 3-(2'-methyl-5'-furyl)propen-2-al — should lead to formation of one and the same bicyclic product — 2-methyl-1,6-dioxaspiro-(4,4)-nonane.

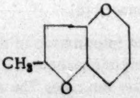


(where R=H or a hydrocarbon radical).



According to the reaction mechanism (formation of dioxa-octahydrindene derivatives) two isomeric compounds (III and IV) should result from the above-indicated furane compounds:


(III)

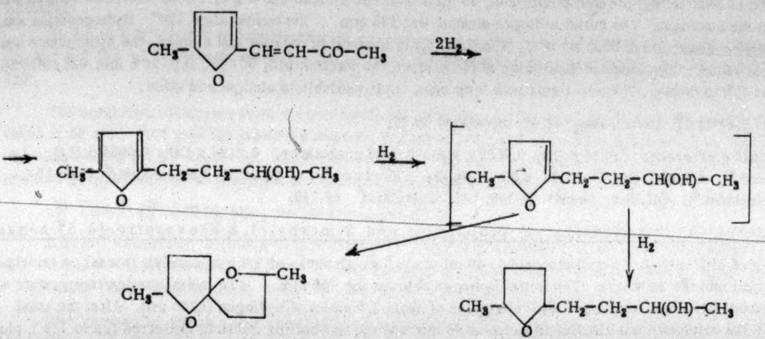

(IV)

Consequently, the synthesis of 2-methyl-1,6-dioxaspiro-(4,4)-nonane from 3-(2'-methyl-5'-furyl)-propen-2-al is a confirmation of both the identity of five-membered rings in molecules of similar compounds, possibly only for the spirane structure, and of the above-given reaction mechanism.

Apparently, in the case of the above-indicated hydrogenation mechanism for 4-(2'-methyl-5'-furyl)-butene-3-one-2, there may also result an accompanying formation of 2,7-dimethyl-1,6-dioxaspiro-(4,4)-nonane, identical with the so-called dimethyloxetone of Fittig obtained from valerolactone [9, 10] and acetonedicarboxylic acid [11]. (see next page).

2,7-Dimethyl-1,6-dioxaspiro-(4,4)-nonane synthesized by such a procedure would be a second representative of this group of compounds obtained from both the furane compound and lactones.

The authors' experiments on two-stage hydrogenation are presented in the present work for 3-(2'-methyl-5'-furyl)-propene-2-al and 4-(2'-methyl-5'-furyl)-butene-3-one-2, as the result of which it has been possible to isolate the corresponding spirocyclic products, identified, respectively, with the spiranes formed by hydrogenation of



furfurylideneacetone, (2-methyl-1,6-dioxaspiro-(4,4)-nonane and the dimethyloxetone of Fittig [2,7-dimethyl-1,6-dioxaspiro-(4,4)-nonane]. Thus, may be considered as experimentally confirmed the earlier-expressed concept concerning spirane structure and their formation mechanism from the corresponding furane aldehydes and ketones or γ-(2-furyl)-alkanols. There have also been obtained the following compounds which have not been described in the literature before, information on which is contained in the experimental part: 3-(2'-methyl-5'-furyl)-propen-2-al, 3-(2'-methyl-5'-furyl)-propanol-1, 3-(2'-methyl-5'-tetrahydrofuryl)-propanol-1, 4-(2'-methyl-5'-furyl)-butanol-2 and 4-(2'-methyl-5'-tetrahydrofuryl)-butanol-2.

EXPERIMENTAL

Hydrogenation was carried out in a steel rotating autoclave, with a capacity of 150 ml. The given temperature was maintained by means of an electronic-controlled millivoltmeter.

Catalysts: copper chromite was prepared by the usual method [12], nickel on kieselguhr, an industrial catalyst of domestic production. The catalyst, before use, was powdered to a fine powder and reduced by heating in a stream of hydrogen.

Hydrogenation of 3-(2'-methyl-5'-furyl)-propen-2-al*

This reaction was run by condensing 5-methylfurfural [13] with acetaldehyde, according to a method similar to that for producing furylacrolein [14].

In a typical experiment, 35 g of freshly-distilled 5-methylfurfural was added to a solution of 2.2 g of NaOH in 500 ml of water, cooled to 0°, over a period of 10 minutes, after which a solution of 21 g of acetaldehyde in 100 ml of water was added over a period of 3-4 hours. Stirring of the reaction mixture was continued for another 2 hours, and then neutralized with the calculated amount of acetic acid. The product was extracted with three portions of ether, 100 ml each, the ether extract dried with anhydrous sodium sulfate, and the residue, after removal of ether, distilled in vacuo. Upon repeated distillation, 11.5 g (28% of theory) of product was obtained, boiling at 98-100° (4 mm). A yellowish oil with peculiar odor.

0.2104 g substance: 0.5406 g CO_2; 0.1176 g H_2O. 0.2024 g substance: 0.5210 g CO_2; 0.1155 g H_2O. Found %: C 70.23, 70.25; H 6.25, 6.38. $C_8H_8O_2$. Calculated %: C 70.57; H 5.92.

Semicarbazone: white, well-developed needles, m.p. 191°.

3-(2'-Methyl-5'-furyl)propen-2-al condenses with ketones, similarly as with furylacrolein. Thus, for example, upon condensing two moles of aldehyde with cyclohexanone, the ketone $C_{22}H_{22}O_3$ is formed, orange crystals with m.p. 168-168.5°.

0.1050 g substance: 0.3024 g CO_2; 0.0648 g H_2O. 0.1188 g substance: 0.3486 g CO_2; 0.0722 g H_2O. Found %: C 78.59, 78.70; H 6.91, 6.80. $C_{22}H_{22}O_3$. Calculated %: C 79.01; H 6.63. Found: M 345.8. Calculated: M 334.4.

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* M D. Lipanova participating.

3-(2'-Methyl-5'-furyl)-propanol-1

18 g of 3-(2'-methyl-5'-furyl)-propen-2-al, 40 ml of absolute alcohol and 3 g of copper chromite catalyst were placed in the autoclave. The initial hydrogen pressure was 135 atm. the temperature 120°. Hydrogenation was complete after absorption of 5850 ml of H_2 (2 moles). After removal of catalyst and alcohol, the hydrogenate was distilled in vacuo. Upon repeated distillation of the product, the fraction with 97-98°, b.p. at 8 mm was collected. Yield was 75% of theory. Colorless liquid with faint odor, readily soluble in alcohol and ether.

n_D^{20} 1.4775; d_4^{20} 1.0322; MR_D 38.42; calculated 39.17.

0.0915 g substance: 0.2285 g CO_2; 0.0682 g H_2O. 0.0873 g substance: 0.2184 g CO_2; 0.0665 g H_2O. Found %: C 68.15, 68.27; H 8.34, 8.53. $C_8H_{12}O_2$. Calculated %: C 68.52; H 8.62. Found %: OH 10.0. Calculated %: OH 12.0. Found: M 142, 147. Calculated: M 140.

3-(2'-Methyl-5'-tetrahydrofuryl)-propanol-1 and 2-methyl-1,6-dioxaspiro-(4,4)-nonane

24 g of 3-(2'-methyl-5'-furyl)-propanol-1, 40 ml of absolute alcohol and 1.2 g of catalyst (nickel on kieselguhr) were charged into the autoclave. The initial hydrogen pressure was 150 atm. The hydrogenation temperature was 120°. Hydrogenation was terminated after absorption of about 1.5 moles of hydrogen (5200 ml). After the usual treatment, the catalysate was distilled in vacuo at 46 mm and the low-boiling fractions collected (up to 110°), plus a fraction with b.p. 111-113°, weighing 15.3 g (yield 63.5%), representing methyltetrahydrofurylpropanol. A colorless liquid with faint odor.

n_D^{20} 1.4635; d_4^{20} 0.9972; MR_D 39.87; calculated 40.11.

0.1020 g substance: 0.2480 g CO_2; 0.922 g H_2O. Found %: C 66.35; H 11.15. $C_8H_{16}O_2$. Calculated %: C 66.62; H 11.18. Found: M 147, 150. Calculated: M 144.2. Found %: OH 11.88. Calculated %: OH 11.80.

To increase the product, the experiment was repeated under the same conditions with the same amounts of initial alcohol, solvent and catalyst.

The low-boiling fractions of both experiments, as well as the residue after repeated distillation through an efficient fractionating column of the solvent distilled off from the catalyzate were combined and redistilled through the fractionating column at atmospheric pressure, as the result of which 7.5 g of fraction, with b.p. 162-164°, was isolated (yield was 15.6% of theory).

Found: M 140.0, 136.8. Calculated: M 142.19. n_D^{25} 1.4412; n_D^{20} 1.4428; d_4^{20} 0.9920; MR_D 37.99; calculated: 38.08.

According to the literature data [5, 6]: 2-methyl-1,6-dioxaspiro-(4,4)-nonane had the following physical constants: n_D^{25} 1.4412 d_4^{25} 0.985; b.p. 157-159°, 80° at 46 mm.

Hydrogenation of 4-(2'-Methyl-5'-furyl)-buten-3-one-2

4-(2'-Methyl-5'-furyl)-buten-3-one-2 was obtained by condensing 5-methylfurfural with acetone in the presence of NaOH [15], b.p. 105.5-107° at 4 mm, m.p. 35-36°. Yield was 61.1% of theory.

4-(2'-Methyl-5'-furyl)-butanol-2

In a typical experiment, 28.5 g of 4-(2'-methyl-5'-furyl)-buten-3-one-2, 40 ml of absolute alcohol and 3 g of copper chromite catalyst were charged into the autoclave and hydrogenated at 120° and an initial hydrogen pressure of 88-95 atm. For accumulation of material, hydrogenation was carried out 5 times for a total amount of 129.9 g of initial ketone. The combined catalyzate from 5 experiments was freed from catalyst and solvent, and then distilled in vacuo at 55 mm. 107.5 g of product resulted, boiling at 136.5-138°, a colorless liquid with faint odor, miscible with standard organic solvents. Yield was 80.5%.

n_D^{20} 1.4760; d_4^{20} 1.000; MR_D 43.49; calculated 43.80.

0.0662 g substance: 0.1706 g CO_2; 0.0559 g H_2O. 0.1732 g substance: 0.4458 g CO_2; 0.1443 g H_2O. Found %: C 70.26, 70.20; H 9.45, 9.32. $C_9H_{14}O_2$. Calculated %: C 70.09; H 9.15.

Found: M 154.7. Calculated: M 154.2. Found %: OH 11.8, 11.7. Calculated %: OH 11.03.

4-(2'-Methyl-5'-tetrahydrofuryl)-butanol-2 and 2,7-dimethyl-1,6-dioxaspiro-(4,4)-nonane.

91.7 g of 4-(2'-methyl-5'-furyl)-butanol-2 was hydrogenated four times for a total of 4.7 g of copper chromite catalyst and 184 ml of absolute alcohol. The initial hydrogen pressure was 130 - 145 atm. The temperature was 120°.

The combined catalyzate from 4 experiments was freed from catalyst and solvent and then redistilled in vacuo at 46 mm. 8.65 g of the substance resulted, boiling at 130°, and the main fraction with b.p. 134 - 136°, weighing 69.35 g (73.6% of theory), which was found to be 4-(2'-methyl-5'-tetrahydrofuryl)-butanol-2. Upon repeated distillation, the boiling point of the product remained constant.

n_D^{20} 1.4542; d_4^{20} 0.9574; MR_D 44.76; calculated 44.73.

0.0770 g substance: 0.1938 g CO_2; 0.0773 g H_2O. 0.0956 g substance: 0.2401 g CO_2; 0.0959 g H_2O. Found %: C 68.48, 68.48; H 11.24, 11.16. $C_9H_{18}O_2$. Calculated %: C 68.31; H 11.47. Found: M 169.2. Calculated M 158.2. Found %: OH 11.27. Calculated %: OH 10.74.

The low-boiling fraction was redistilled at atmospheric pressure. Because it was not possible to narrow down the boiling range (168 - 175°) of the small fraction, despite repeated distillation, the boiling point of the product was more precisely determined according to Emich [16], and was found to be 167 - 169°. Weight was 2.87 g.

n_D^{20} 1.4389; d_4^{20} 0.9594; MR_D 42.82; calculated 42.65.

0.1215 g substance: 0.3070 g CO_2; 0.1111 g H_2O. 0.1192 g substance: 0.3001 g CO_2; 0.1099 g H_2O. Found %: C 68.92, 68.66; H 10.23, 10.32. $C_9H_{16}O_2$. Calculated %: C 69.19; H 10.32. Found: M 149.5. Calculated: M 156.2.

The product did not show the presence of hydroxyl groups; it gave a silver mirror with an ammoniacal silver oxide solution. It formed white crystals with hydrogen bromide, m.p. 41 - 42°, and possessed a very pleasant odor.

According to the literature data [9, 10]: the Fittig dimethyloxetone has a b.p. of 169.5°; 167 - 169°; d_0^0 0.978; it forms a silver mirror with an ammoniacal solution of silver oxide; it possesses a terpene odor. The interaction product with HBr melts at 42°.

SUMMARY

1. As the result of catalytic hydrogenation of 3-(2'-methyl-5'-furyl)-propene-2-al and 4-(2'-methyl-5'-furyl)-butene-3-one-2 there have been obtained 3-(2'-methyl-5'-furyl)-propanol-1, 3-(2'-methyl-5'-tetrahydrofuryl)-propanol-1, 4-(2'-methyl-5'-furyl)butanol-2 and 4-(2'-methyl-5'-tetrahydrofuryl)-butanol-2, as well as 2-methyl-1,6-dioxaspiro-(4,4)-nonane and 2,7-dimethyl-1,6-dioxaspiro-(4,4)-nonane.

2. It has been demonstrated that the formation of 2-methyl-1,6-dioxaspiro-(4,4)-nonane from 3-(2'-methyl-5'-furyl)-propene-2-al by catalytic hydrogenation constitute a new synthetic proof, both of the structure for spiranes of this type, and for their formation mechanism from furfurylidene aldehydes and ketones and γ-(2-furyl)-alkanols as accepted by the authors.

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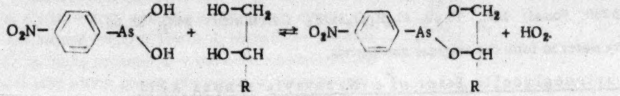
α-GLYCOLIC ESTERS OF p-NITROPHENYL-ARSENOUS AND α-NAPHTHYL-ARSENOUS ACIDS

Gilm Kamai and N. A. Chadaeva

The present work is a continuation of the authors' investigations in the field of cyclic glycolic esters of arsenous and arylarsenous acids. Here work has been undertaken to study the method of synthesis of certain cyclic α-glycolic esters of p-nitrophenyl-arsenous and α-naphthyl-arsenous acids.

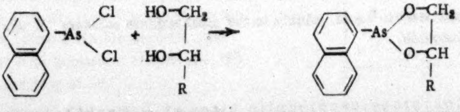
By action of an equimolecular quantity of p-nitrophenylarsenous acid upon various α-glycols (with heating), α-glycolic esters of p-nitrophenylarsenous acid were synthesized according to the following equation:



where: R=H or CH_2OCH_3, $CH_2OC_2H_5$.

Thus, the ethyleneglycolic, α-methoxypropyleneglycolic and α-ethoxypropyleneglycolic esters of p-nitrophenylarsenous acid were isolated, readily hydrozable by water.

The α-glycolic esters of α-naphthylarsenous acid were obtained by the authors through the interaction of α-naphthyldichloroarsine with the corresponding α-glycols in absolute ether medium with the presence of pyridine, according to the equation:



The resulting α-glycolic ester of α-naphthylarsenous acid was a viscous, transparent liquid, unstable in the air, hydrolyzing to form α-naphthylarsineoxide.

EXPERIMENTAL

Synthesis of the Ethyleneglycolic Ester of p-Nitrophenylarsenous Acid

13 g of vacuum-distilled p-nitrophenylarsenous acid and 12 g of freshly-distilled ethylene glycol were placed in an Arbuzov distilling flask. The apparatus was put under vacuum, and the flask contents then carefully heated on an oil bath. Drops of reaction water were observed on the walls of the flask at a bath temperature of about 80°. The distillation was carried out at constant vacuum. Two fractions were isolated:

1st, B.p. 98-100° at 12 mm – 7.2 g; 2nd, B.p. 170-174° at 5 mm – 7.8 g.

The second fraction solidified upon standing. After recrystallization from carbon tetrachloride, the crystals melted at 119-121°.

Found %: As 28.89, 28.93. $C_8H_8O_4AsN$. Calculated %: As 29.14.

The resulting ester was represented as light-yellow crystals, readily soluble indivers organic solvents; hydrolyzed by water, forming p-nitrophenylarsenous acid.

Synthesis of the α-Methoxypropyleneglycolic Ester of p-Nitrophenylarsenous Acid

13.6 g of the compound was obtained, with b.p. 188-190° at 2 mm (with partial decomposition) from a mixture of 22 g of α-methoxypropyleneglycol and 21.3 g of p-nitrophenyl-arsenous acid in a manner similar to that described above.

Found %: As 25.15, 25.08. $C_{10}H_{12}O_5AsN$. Calculated %: As 24.88.

The ester obtained was represented by light-yellow, hygroscopic crystals, with m.p. 54-55°, readily soluble in organic solvents. It was readily hydrolyzed by water.

Hydrolysis of the α-Methoxypropyleneglycolic Ester of p-Nitrophenylarsenous Acid.

3 g of the ester under investigation was dissolved in 15 ml of 20% sodium hydroxide. The solution was filtered off and neutralized with 15% hydrochloric acid. The precipitated fine yellow crystals were filtered off and washed repeatedly with water. After drying to constant weight, the crystals were analyzed.

Found %: As 32.38, 32.53. $C_6H_6O_4AsN$. Calculated %: As 32.42.

The crystals were found to be p-nitrophenylarsenous acid.

Synthesis of the α-Ethoxypropyleneglycolic Ester of p-Nitrophenylarsenous acid.

The ester was obtained by interacting 10 g of p-nitrophenylarsenous acid with 14 g of α-ethoxypropyleneglycol. B.p. 184-185° at 3 mm. The yield of pure compound was 5.2 g.

Found %: As 23.51, 23.64. $C_{11}H_{14}O_5AsN$. Calculated %: As 23.87.

The ester was a yellowish-green, viscous liquid, readily soluble in the standard solvents:

d_4^{20} 1.4793; n_D^{20} 1.5700. Found: MR_D 70.49. $C_{11}H_{14}O_5AsNF_3$. Calculated: MR_D 68.36.

It was hydrolyzed by water to form the original compounds.

Synthesis of the Ethyleneglycolic Ester of α-Naphthylarsenous Acid.

14 g of α-naphthyldichloroarsine dissolved in 100 ml of ethyl ether was added through a dropping funnel, with stirring, to a solution, pre-cooled to 0°, of 4 g of ethylene glycol and 7.9 g of anhydrous pyridine in 350 ml of absolute ether. Having introduced the total amount of α-naphthyldichloroarsine, the flask contents were then heated on a water bath for 30 minutes. After cooling, the precipitate of pyridine hydrochloride was filtered off, washed with ether, the solvent distilled off, and the remaining liquid fractionated in vacuo. 5.55 g of the compound, with b.p. 169-170° at 4 mm resulted.

Found %: As 28.44, 28.65. $C_{12}H_{11}O_2As$. Calculated %: As 28.65.

The ester was a transparent, viscous liquid, soluble in the usual organic solvents. It was readily hydrolyzed by water to form α-naphthylarsineoxide.

d_4^{30} 1.5043; n_D^{30} 1.6677.

Synthesis of the α-Methoxypropyleneglycolic Ester of α-Naphthylarsenous Acid

This compound was isolated by the method described above, proceeding from the corresponding α-glycol, 7.9 g of dry pyridine, 400 ml of ethyl ether, and 14 g of α-naphthyl-dichloroarsine. The b.p. was 185-186° at 3 mm. Yield was 7 g.

Found %: As 24.15, 24.21. $C_{[illegible]}H_{15}O_3As$. Calculated %: As 24.47.

The ester — a viscous, transparent liquid: d_4^{20} 1.4209, n_D^{20} 1.6282. Hydrolyzing in moist air to form α-naphthylarsineoxide, with m.p. 245°.

SUMMARY

1. Various α-glycolic esters of p-nitrophenylarsenous and α-naphthylarsenous acids were synthesized and some of their properties have been studied.

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* See Consultants Bureau English Translation, page 807.

REACTION OF NITRATES AND NITRITES OF METALS OF THE FIRST AND SECOND GROUPS OF THE D. I. MENDELEEV PERIODIC SYSTEM IN MELTS

VII. INVESTIGATION OF THE TERNARY SYSTEM LITHIUM, POTASSIUM, AND THALLIUM NITRATES

P. I. Protsenko and I. K. Shelomov

Chemical compounds of monovalent thallium resemble those of the metals of the first group of the D. I. Mendeleev periodic system in all of their physico-chemical properties But in view of certain individual peculiarities of lithium, which differentiate it from the alkali metals, it seemed important to study the reaction of thallous nitrate with lithium nitrate, and to determine whether or not the above analogy was retained in melts with lithium nitrate.

For the above reason, and also to gather material on the nitrate-nitrite equilibrium of metals of the first and second group of the D. I. Mendeleev periodic system in melts, necessary for the determination of the general laws which govern the course of the reaction, the ternary system, lithium, potassium, and thallous nitrates, was investigated by the thermal method of physico-chemical analysis.

Binary Systems. Structural diagrams of the system potassium nitrate-thallous nitrate were investigated by A. G. Bergman [1], A. P. Rostkovsky [2], P. K. Leman [3], and others. A repeat investigations by the authors confirmed the general character (Fig. 1). Thallous nitrate does not react chemically with potassium nitrate but forms a simple eutectic containing 28 molecular % of potassium nitrate and 72% of thallous nitrate * melting at 181°.

The diagram of the system lithium nitrate-potassium nitrate was previously studied and reported by one of the authors [4] (Fig. 1). It also shows a complete eutectic containing 58% of potassium nitrate, and 42% of lithium nitrate, melting at 120°.

The structural diagram of the binary system thallous nitrate-lithium nitrate was newly studied by the authors. The liquidus curve of this system consists of the crystallization of thallous nitrate and crystallization of lithium nitrate branches. The eutectic point corresponds to a composition 70.5% of thallous nitrate and 29.5% of lithium nitrate.

It could be supposed from the character of the binary systems which are the primary constituents of the ternary system potassium-thallous-lithium nitrates, that no chemical reaction between the above components would occur within the ternary system, which was indeed confirmed experimentally.

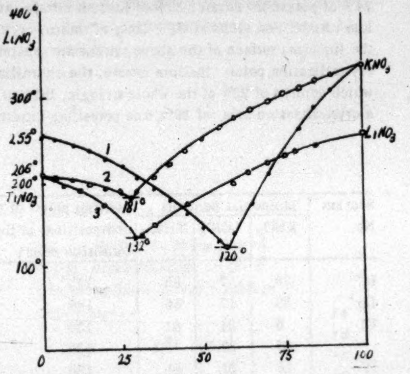

Fig. 1. Binary Systems. 1 – $LiNO_3$-KNO_3, 2 – $TlNO_3$-KNO_3, 3 – $TlNO_3$-$LiNO_3$.

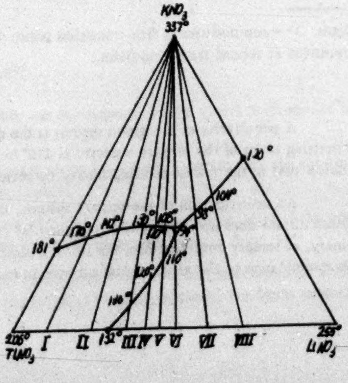

Fig. 2. Direction of sections of the ternary system.

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* Subsequently the composition is expressed in molecular per cent.

Sections of the Ternary System. In order to study the liquidus surface of the ternary system potassium-thallous-lithium nitrates, 8 sections were investigated, the character and direction of which are shown in Fig. 2. As it is apparent from this figure, all of the sections have the direction from the side thallous nitrate-lithium nitrate to the apex potassium nitrate. Structural diagrams for the sections are given in Figs. 3, 4, and 5.

The crystallization surface was shown (Fig. 6) by means of a projection of the isotherm triangle from the given sections and binary systems. The isotherms were taken through 20°. The composition of the ternary section was found experimentally and was confirmed by an orthogonal projection of the mutual crystallization curves on the side of the triangle, thallous nitrate-lithium nitrate (Fig. 7). The structural diagram of the ternary system thallous, lithium, and potassium nitrates belong to those of the simplest type with a ternary eutectic. The ternary eutectic point corresponds to the composition 34% of potassium nitrate, 33% of lithium nitrate, and 33% of thallous nitrate, and melts at 94°. Lines of mutual crystallization on the liquidus surface of the above system are separated into three crystallization poles: thallous nitrate, the crystallization area of which consists of 22% of the whole triangle, lithium nitrate with a crystallization area of 39%, and potassium nitrate, 39%.

Section No.	Molecular percents			Melting points of the compositions at the transition points
	KNO_3	$LiNO_3$	$TlNO_3$	
Ia*	30	7	63	170°
IIb*	33	17	50	142
III a*	5	34	61	130
b*	35	22.5	43.5	130
IV a*	15	34	51	120
b*	36	26	38	120
V	25	34	41	110
	34	30	36	108
VI	34	33	33	94

Notes. a* – composition at first transition point; b* – composition at second transition point.

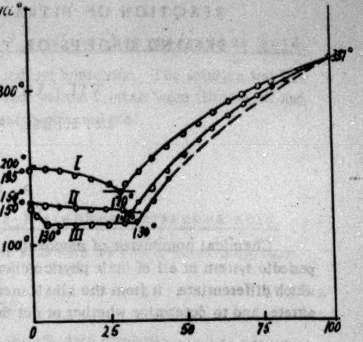

Fig. 3. Sections through the ternary system.

I – 90% $TlNO_3$ + 10% $LiNO_3$ → KNO_3.
II – 75% $TlNO_3$ + 25% $LiNO_3$ → KNO_3.
III – 65% $TlNO_3$ + 35% $LiNO_3$ → KNO_3.

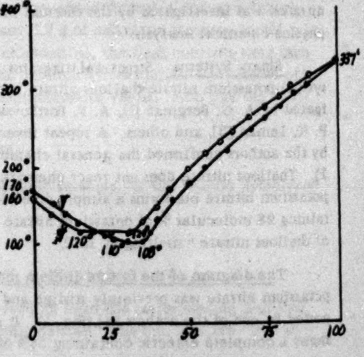

Fig. 4. Section through the ternary system.

IV – 60% $TlNO_3$ + 40% $LiNO_3$ → KNO_3.
V – 55% $TlNO_3$ + 45% $LiNO_3$ → KNO_3.

A peculiarity of the given system is the exceptionally low melting point of the ternary eutectic, 94°. The melting point of the ternary eutectic is 112° below that of the lowest melting component of the system, and 26° below that of the lowest melting binary eutectic consisting of lithium and potassium nitrates.

An investigation of the ternary system, thallous, lithium, and potassium nitrates, showed that monovalent thallium nitrate does not display any tendency for chemical reaction with lithium and potassium nitrates, either in binary, or ternary combinations, but forms a simple eutectic mixture with them. Thallous nitrate shows a complete resemblance to the alkali metal nitrates in melts.

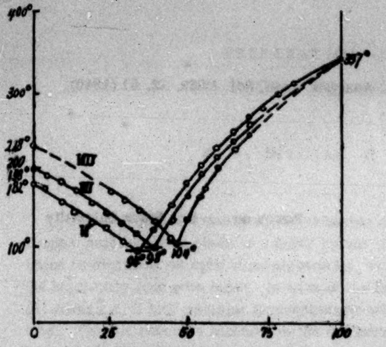

Fig. 5. Sections through the ternary system.
VI − 50% $TlNO_3$ + 50% $LiNO_3$ — KNO_3;
VII − 40% $TlNO_3$ + 60% $LiNO_3 \rightarrow KNO_3$;
VIII − 25% $TlNO_3$ + 75% $LiNO_3 \rightarrow KNO_3$.

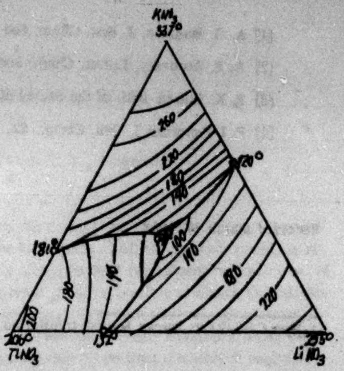

Fig. 6. Projection of the crystallization surface of the ternary system based on a triangle.

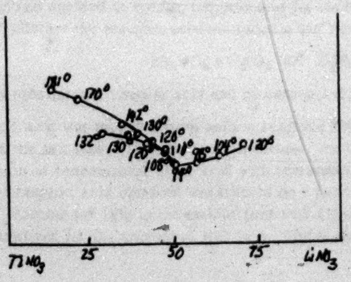

Fig. 7. Projection of the line of mutual crystallization on the side of thallium nitrate – lithium nitrate side.

SUMMARY

1. The ternary system thallous-lithium-potassium nitrates was investigated by the visual polythermic method of physico-chemical analysis.

2. The binary system thallous nitrate-lithium nitrate studied showed a simple eutectic with the melting point 132° containing 70.5% thallous nitrate and 29.5% lithium nitrate.

3. It was shown that the ternary system belongs to those with one ternary non-variant point of the composition: 34% potassium nitrate, 33% lithium nitrate, and 33% thallous nitrate, and melting point 94°.

4. It was shown that thallous nitrate, because of its great resemblance in all of its physico-chemical properties to lithium and potassium nitrates, does not participate in chemical reaction in melts, but forms eutectic mixtures with them in binary, as well as ternary systems.

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PREPARATION OF PHOSPHOTUNGSTIC ACID FROM PHOSPHORIC AND TUNGSTIC ACIDS

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An analysis and experimental evaluation of literature results on the methods for the preparation of phosphotungstic acid has been given in a paper by one of the authors [1]; the best results of all the methods tested, in relation to obtaining an individual preparation, were given by the ether procedure with two subsequent treatments of the heteropoly acid with ether. In spite of the fact that the above method makes it possible to obtain the individual substance, it still contains inconveniences which are inevitable when one works with such volatile solvents as ether. For this reason, a method for the synthesis of phosphotungstic acid was subsequently developed which circumvented the stage of the formation of its etherate. Rosenheim [2] considers that "the direct synthesis of heteropolyacids is only possible in exceptional cases, as for example, with luteo compounds and only with poor yields."

An attempt for the direct synthesis of phosphotungstic acid from tungstic anhydride and phosphoric acid in aqueous solution is reported in Hastings and Frediani's paper [3]. In spite of the fact that the authors employed a twofold excess of phosphoric acid in one of the experiments, phosphotungstic acid was not obtained.

It is believed that the lack of success was due to the fact that they used tungstic anhydride for the synthesis, which is a substance with insufficient reactivity.

The authors decided to employ tungstic acid for the synthesis. For this reason it was necessary, first of all, to determine whether the reaction between tungstic and phosphoric acid proceeds according to the equation:

$$12H_2WO_4 + H_3PO_4 \rightleftarrows H_7[P(W_2O_7)_6] + xH_2O$$

Freshly precipitated tungstic acid and phosphoric acid (d 1.511) were used as the starting materials.

Tungstic acid was prepared from sodium tungstate dissolved in water, calculated for a ratio of 1:6 relative to the weight of the salt used. The solution was filtered, and the tungstic acid was precipitated from it by the addition of a thin stream of concentrated nitric acid with continuous stirring until complete precipitation. The white curdy precipitate of tungstic acid obtained was filtered on a porcelain filter and washed with distilled water until the absence of a reaction for NO_3^- in the residue (test with diphenylamine and sulfuric acid). The residue was then sucked and analysed for the amount of H_2O in it. The tungstic acid obtained by this method contained about 20% of WO_3.

The tungstic acid, analyzed for water content, was used for the preparation of phosphotungstic acid.

A weighed sample of about 100 g of tungstic acid of known WO_3 content was placed into a 1 liter round bottom flask. Phosphoric acid, in an amount greater than calculated by the above equation, was added to it.

The total volume of the reaction mixture was brought to about 0.5 liters by the addition of water; the reaction mixture obtained in this manner was boiled for several hours with continuous mechanical stirring, keeping the volume constant. The reaction mixture was then cooled, filtered from the unreacted tungstic acid, and the filtrate evaporated in order to isolate the crystals of phosphotungstic acid.

In the first two experiments, the tungstic acid obtained from 200 g of sodium tungstate was washed with water heated almost to boiling, wherein the filtration of the residue on the funnel was alternated with stirring in a beaker with hot water The initially white, curdy residue became at the end of the washing bright yellow and assumed the form of separate hard granules. Two experiments on the synthesis of phosphotungstic acid were conducted with this yellow preparation. Heating of the reaction mixture lasted for 6 hours in one case, and 15 in the other. But in both cases, the complex formation reaction occurred only to an insignificant degree; much unused tungstic acid remained which passed through the filter during filtration (colloidal tungstic acid). In the second experiment, 15 ml of concentrated hydrochloric acid was added to the reaction mixture before filtration. The solution was boiled, and the residue of the tungstic acid was then completely filtered. The transparent filtrate was evaporated on the water bath until complete removal of the hydrochloric acid, and then to dryness, but no crystals of phosphotungstic acid could be obtained. Only a thin crystalline film of nonvolatile substances was formed on the bottom of the dish, which was washed out from the reagents used.

The yellow monohydrate of tungstic acid was, therefore, practically incapable of participating in a complex formation reaction with phosphoric acid.

A series of orientating experiments was then conducted on the washing of the tungstic acid with water heated to various temperatures in order to determine under what conditions a more reactive tungstic acid would be obtained.

Tungstic acid was precipitated from 200 g of sodium tungstate, filtered on a porcelain filter, and separated into four parts. Each of these was washed until the absence of a reaction for NO'_3 in the residue, with water heated to various temperatures.

250 ml of water was used for each wash. The temperature of the water, the amount of washings, and the external appearance of the washed tungstic acid is given in Table 1.

TABLE 1

Results of the Washing of Tungstic Acid

Expt. No.	Temperature (in °)	Number of washings	External appearance of the washed acid
1	80	4	Yellow, having the form of granules.
2	70	5	Light yellow, almost completely curdy
3	60	6	Light yellow, curdy
4	50	6	" " "

At the end of the washing, all four of the residues were placed into flasks, and 2 ml of phosphoric acid and 150 ml of water added to them; the solutions obtained were boiled for 2 hours, cooled to room temperature, and the volume of all of the solutions adjusted to 100 ml.

In order to determine in what case the complex formation reaction proceeded the most completely, the following method was used: 15 ml of the solution was removed from each flask and 5 ml of quinoline acetate added to each. By the size of the precipitate formed, it could be judged in which solution more of the complex anion could be found. The amount of precipitate was approximately equal for the last three samples, and considerably less in the first.

In subsequent experiments the washing of the tungstic acid was effected with water heated to 60-70°.

Later, a series of experiments was conducted in order to determine how much the reactivity of the tungstic acid changes with time (aging).

Tungstic acid was prepared from 500 g of sodium tungstate, washed, and analyzed for the amount of water in it.

Part of the tungstic acid was used for the preparation of phosphotungstic acid directly after the washing, the second experiment with the same tungstic acid was conducted after one day, the third, after two days, and the fourth three days after the washing of the starting preparation. Before each experiment, the tungstic acid was carefully mixed and analyzed for the amount of H_2O. The phosphoric acid was added in an amount based on the amount of WO_3 used, according to the equation:

$$12WO_3 + H_3PO_4 + xH_2O \rightleftarrows H_7[P(W_2O_7)_6].$$

The volume of the reaction mixture in all experiments was adjusted to 0.5 liters by the addition of water; the boiling with continuous stirring and constant volume (periodic addition of water) lasted for 6 hours.

In all experiments, part of the tungstic acid did not react; very little of it remained in the first experiment, in comparison to the others The amount of H_2WO_4 noticeably increased from the first to the fourth experiment

The residue was filtered through a double thickness filter (the filtrates all were cloudy), and was analyzed for the amount of water in it after weighing.

The amount of starting tungstic acid remaining in the residue, as well as the per cent WO_3 used, is given in Table 2.

From the data in Table 2, it is apparent that the reactivity of tungstic acid is greatly diminished with aging. It is necessary to use tungstic acid for complex formation directly after the washing

As it was stated above, the solution at the end of the synthesis, filtered poorly because the remaining tungstic acid passed through the filter A series of experiments was conducted to determine conditions under which the precipitate could be separated completely.

The filtrates obtained in experiments 2, 3, and 4 (Table 2) were combined, mixed well, and filtered under various conditions; namely, through one-and two-sheet paper filters on a porcelain filter, and through the same amount of filters on the usual funnel; the filtrate was always cloudy but somewhat clearer in the last case. The

TABLE 2

Effect of Aging of Tungstic Acid on the Process of Complex Formation

Expt. No.	Time between the preparation of H_2WO_4 and its use for the complex formation reaction	Used for the synthesis (in g)		Remaining (in g)		Percent WO_3 used
		Moist H_2WO_4	Amount of WO_3	Moist H_2WO_4	Amount of WO_3	
1	Directly after washing	115	20.9	6	1.67	92.0
2	18 hours	108	20.4	42	7.0	65.7
3	2 days	117	23.0	68	13.5	41.3
4	3 days	111	22.3	83	16.0	28.2

filtration without vacuum proceeded slowly; then a paper filter was placed on a porcelain funnel and a thin dense layer of washed tungstic acid placed upon it, which served as a filter. The residue was retained completely in this case.

As it was established, the reaction between tungstic and phosphoric acids does not go to completion. For this reason the filtrate, in addition to the phosphotungstic acid, contains some free phosphoric acid. In order to obtain pure preparations, a crystallization has to be effected in the presence of the mother liquor which is difficult because the acid is very soluble in water and crystallizes with a large number of molecules of water.

Experiments conducted showed that it was best to evaporate the filtrate until the appearance of the first crystals on the surface of the solution or on the bottom of the dish; then the solution must be cooled to room temperature, and the deposited crystals of phosphotungstic acid must be separated at once. If the above is not done, an almost continuous mass of fine crystals is formed which is difficult to separate from the mother liquor.

From the filtrate obtained in experiment 1, Table 2, 14.5 g of crystals was isolated which were then recrystallized; 8.1 g of phosphotungstic acid was obtained The P_2O_5 content in it amounted to 2.47%, based on the anhydrous preparation (theoretical yield 2.49%).

Therefore, pure phosphotungstic acid can be obtained by means of the above method.

Therefore, conditions were found as a result of the experiments conducted, under which the reaction between tungstic and phosphoric acids proceeded to a sufficient degree of completion, and a method for the preparation of phosphotungstic acid without the use of ether was developed.

The recommended method consists of the following: tungstic acid is precipitated from a solution of sodium tungstate with the aid of nitric acid, which is filtered and washed with distilled water heated to 60 – 70° until a negative reaction for NO_3' in the residue. The acid obtained is analyzed for the amount of water in it, and is used at once for the preparation of phosphotungstic acid. The synthesis is conducted as reported above. At the end of the synthesis, in order to hasten the filtration, the solution is evaporated to $^3/_4$ of the volume and filtered while hot through a thin layer of washed tungstic acid. The transparent filtrate is evaporated until the appearance of the first crystals, and the isolation of these is effected as stated above.

Two samples of phosphotungstic acid were prepared by means of the proposed method.

The amount of tungstic acid used, the yield, and the results of analysis of the samples obtained are given in Table 3.

TABLE 3.

Results of Experiments on the Preparation of Phosphotungstic Acid

Sample No.	Used (in g)		Remaining (in g)		% WO_3 used	Heteropolyacid obtained (in g)		% Yield based on WO_3 reacted	P_2O_5 in the phosphotungstic acid (in %)	Amount of mother liquor (in ml)
	Moist H_2WO_4	WO_3	Moist H_2WO_4	WO_3		Hydrate	Anhydrous			
1	360	79.2	32	7.2	91	27.4	23.6	32.7	2.46	1 – 12 2 – 5
2	540	91.8	68	12.0	87	32.8	27.2	34.1	2.52	1 – 17 2 – 6

The yield of the heteropolyacid is given in relation to the tungstic acid reacted.

It is better to evaporate the mother liquors separately. The amount of phosphoric acid remaining in the mother liquor increases with the separation of the crystals of phosphotungstic acid; they must be combined with the initial solution for the synthesis of phosphotungstic acid.

The remaining tungstic acid was placed into a flask and H_3PO_4 was added to it in a quantity greater than necessary, by calculation, for the preparation of the heteropoly acid, and the mixture boiled for two hours; about 2% of the tungstic acid used reacted. Therefore, the remaining tungstic acid is not very reactive and cannot be used directly for the synthesis of phosphotungstic acid; it must be reconverted with sodium hydroxide into sodium tungstate and the solution obtained combined with the sodium tungstate solution for the separation of tungstic acid from it for a new synthesis of the compounds.

P_2O_5 was determined in the form of magnesium pyrophosphate; the precipitation of the ammonium magnesium phosphate salt was effected during the cooling of the solution to 3-5°; the tungsten was precipitated with quinoline after the removal of the P_2O_5.

For the determination of Na_2O, the heteropolyanion was precipitated with quinoline acetate, and the sodium determined as Na_2SO_4; the water determined by heating a sample to constant weight.

SUMMARY

1. Conditions were found for the preparation and washing of tungstic acid capable of a complex formation reaction with phosphotungstic acid; it was shown that the ability of tungstic acid for complex formation changes with time.

2. A new method for the direct synthesis of phosphotungstic acid from phosphoric and tungstic acids without the use of ether was developed.

3. Methods are given for the use of waste products: unreacted tungstic acid and the mother liquors containing excess phosphoric acid.

4. The yield of the preparation was about 33% based on the tungstic acid reacted.

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INVESTIGATIONS OF POLYTHIONIC ACIDS

II. HYDROLYSIS OF SULFUR DICHLORIDE

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Almost all of the investigators working recently on the chemistry of polythionic acids agree that these acids are formed by means of some unstable intermediate substance from other sulfur compounds. Among these unstable intermediate substances, the hypothetical hydrosulfurous acid must be of great importance, as was shown, even in 1935, by one of the authors [1]. This suggestion was confirmed experimentally by Goehring by the hydrolysis of esters and alkyl amides of hydrosulfurous acid [2]. Goehring found pentathionic acid among the products of the hydrolysis of diethyl hydrosulfite; the semi-quantitative character of her experiments, however, does not allow a conclusion to be made on the mechanism of the formation of the final products of the spontaneous decomposition of hydrosulfurous acid.

Sulfur dichloride can be considered a derivative of hydrosulfurous acid; i.e., its acid chloride. For this reason it could be expected that the primary products of the reaction of sulfur dichloride with water would be hydrogen chloride and the unstable hydrosulfurous acid, and that an analytical study of the isolated products of the hydrolysis of sulfur dichloride under various conditions would throw light on the reactions of hydrosulfurous acid, and in particular, those leading to the formation of polythionic acid.

The aim of the present investigation was the systematic study of the hydrolysis of sulfur dichloride, mainly on the relation of the hydrolysis products to the acidity of the medium, which is very important as is known [1] for the formation of polythionic acids.

Experimental method. Specially prepared sulfur dichloride containing 32.0% S and 68.0% Cl was used as the starting material. Certain deviations from the stoichiometric composition of SCl_2 (31.1% S and 68.9% Cl), were predicted by the fact that sulfur dichloride, although slowly, dissociates partly according to the equation [3]:

$$2SCl_2 \rightleftharpoons S_2Cl_2 + Cl_2. \tag{1}$$

For this reason, a small excess of sulfur over the stoichiometric composition, in other words, a small impurity of S_2Cl_2 was necessary to avoid a considerable shift of this equilibrium to the right. The sulfur dichloride prepared was stored at 0° in sealed ampoules.

Experiments on the hydrolysis were conducted in the following manner: A sealed ampoule, with an accurately known amount of sulfur dichloride, was placed into a thick-walled bottle and covered with water, or the solution of the desired composition. The ampoule was broken by energetic shaking of the hermetically sealed bottle, which signified the start of the reaction. The end of the hydrolysis was readily established visually as the liquid sulfur dichloride is not miscible with water. A considerable amount of colloidal sulfur separates during the course of the reaction. After its coagulation by means of lanthanum or aluminum chloride, the reaction mixture was filtered through a tared filter; the filtered and washed sulfur was dried at room temperature in a desiccator and weighed. The mother liquor was subjected to quantitative analysis [4].

Hydrolysis of sulfur dichloride in pure water. The results of four experiments are given in Table 1, in which 5 – 10 g of SCl_2 was hydrolyzed in 400 – 500 ml of pure water. The analysis of the reaction mixture was effected in separate experiments after several intermediate times (4 – 19 hours) from the start of the reaction. The results are more conveniently expressed as the per cent sulfur found in the form of the isolated reaction products in a ratio to the total starting amount.

The experiments of this series show that the predominant reaction products are pentathionic acid and elementary sulfur. The relative amount of pentathionic acid decreases with time, and that of sulfur increases. This undoubtedly results from the slow decomposition of pentathionic acid [5]. Tetra and trithionic acids must also be considered as products of the decomposition of pentathionic acid, small quantities of which were found in experiment 4; i.e., 19 hours from the start of the hydrolysis of sulfur dichloride. The absence of both these acids in the first three experiments leaves no doubt that the first of the polythionic acids was pentathionic acid.

It is also important that in all experiments thiosulfuric acid was found, although in small amounts. This enables the mechanism of the basic reaction, the formation of pentathionic acid, to be expressed by the equations:

TABLE 1

Hydrolysis of Sulfur Dichloride in Pure Water

Expt. No.	1		2		3		4	
SCl_2 used (in g)	4.369		9.640		7.365		8.142	
Hydrolysis time* (in hrs)	4		12		15		19	
Reaction products	Milli-moles	% S	Milli-moles	% S	Milli-moles	% S	Milli-moles	% S
H_2SO_3	0.41	0.9	0.63	0.7	0.32	0.4	2.98	3.7
$H_2S_2O_3$	0.585	2.7	0.48	1.0	0.32	0.9	0.165	0.4
$H_2S_3O_6$	0	0	0	0	0	0	1.94	7.1
$H_2S_4O_6$	0	0	0	0	0	0	0.52	2.6
$H_2S_5O_6$	6.826	77.9	13.66	70.1	9.51	64.6	6.87	42.2
H_2SO_4	3.02	6.9	3.23	3.3	4.33	5.9	7.90	9.7
S	5.66**	13.0	23.28**	24.2	20.81**	28.2	29.43**	36.1

$$SCl_2 + 2H_2O \rightarrow S(OH)_2 + 2HCl \qquad (2)$$

$$2S(OH)_2 \rightleftarrows H_2S_2O_3 + H_2O \rightleftarrows 2H^{\cdot} + S_2O_3^{''} + H_2O \qquad (3)$$

$$S(OH)_2 + 2H_2S_2O_3 \rightarrow H_2S_5O_6 + 2H_2O \qquad (4)$$

The amount of elementary sulfur formed in all experiments, however, was too great to be explained by the decomposition of pentathionic acid. The usual decomposition of thiosulfuric acid

$$H_2S_2O_3 \rightarrow S + SO_2 + H_2O \qquad (5)$$

cannot be of much significance here since in all cases the reaction mixture contained only very small amounts of sulfur dioxide. In addition, the latter can also be the product of the decomposition of polythionic acids. Therefore, elementary sulfur must be a waste product of a side reaction occurring parallelly with the formation of pentathionic acid.

The constant presence of considerable amounts of sulfuric acid in the reaction mixture had to be kept in mind. Sulfuric acid cannot be a decomposition product of polythionic acids in the given case, since significant amounts of sulfate ions are formed by the decomposition of trithionic acid [5], which was not found in any quantity in the first three experiments. Therefore, sulfuric acid also is a product of a side process which accompanies the formation of pentathionic acid.

A study of the reaction of esters of hydrosulfurous acid with various reducing agents [2] showed that hydrosulfurous acid possesses strong oxidizing properties in addition to its long-known reducing properties; the product of its reduction usually is elementary sulfur. The above resulted in speculation that the formation of sulfuric acid, also partially the formation of elementary sulfur in these experiments is the result of one and the same process, the auto oxidation of hydrosulfurous acid

$$3S(OH)_2 \rightarrow H_2SO_4 + 2S + 2H_2O. \qquad (6)$$

In experiments 2 – 4, the amount of sulfur formed was considerably greater than the ratio $S:H_2SO_4 = 2:1$, necessary from this equation. But in experiment 1, in which the analysis of the reaction mixture was conducted a short time after the start of the hydrolysis, this ratio was equal to 1.87:1; i.e., approximately equal to that required by equation (6). In the rest of the experiments of this series, the amount of elementary sulfur increased, evidently, as a result of the slow decomposition of pentathionic acid.

It must also be mentioned that the relative amounts of sulfuric acid found in all of these experiments were of the same order, and even less than found by Goehring [2] during the hydrolysis of ethyl hydrosulfite. Therefore, it must be deemed unnecessary to consider the oxidation of sulfur compounds by chlorine as a possible explanation for the formation of sulfuric acid; i.e., a noticeable dissociation of sulfur dichloride according to equation (1).

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* Time from the start of the experiment to the moment of analysis.

** Amount of S in Tables 1, 2, 3 and 4 is in milli-atoms.

Hydrolysis in acetate buffer. Because hydrochloric acid is formed during the hydrolysis of sulfur dichloride in pure water, the reactions of hydrosulfurous acid leading to the formation of the end products which were detected by analysis, proceeds in strong acidic medium. For this reason, in order to study these reactions in weakly acidic media, sulfur dichloride was hydrolyzed in the subsequent experiments in acetate buffer solution containing a large excess of the buffer substance. The results of one experiment at pH 4.7 (Table 2) are given as an example. From the data of Table 2, it is apparent that a large amount of sulfur dichloride is transformed into polythionic acids; however, in addition to pentathionate, much trithionate and tetrathionate was found. These appear evidently as a result of the large value of the pH relative to that of previous experiments, because the stability of pentathionic acid decreases with the decrease in acidity of the medium, and it decomposes with the formation of the lower polythionate [5].

TABLE 2

Hydrolysis of Sulfur Dichloride at pH 4.7

Expt. No.	5	
used:		
SCl_2 (in g)	4.587	
$NaC_2H_3O_2$ (in milli moles)	225	
$C_2H_4O_2$ (in milli moles)	225	
Hydrolysis time (in hrs)	1	
Reaction products	Milli-moles	% S
SO_3''	0	0
S_2O_3''	3.72	16.2
S_3O_6''	1.56	10.2
S_4O_6''	2.34	20.4
S_5O_6''	2.82	30.7
SO_4''	2.42	5.2
S	8.87	19.3

A more important difference in comparison with the results of hydrolysis in pure water is the presence of very considerable amounts of thiosulfate here. Thiosulfate becomes stable [6] at pH > 4; for this reason there appear to be conditions for the shift of the equilibrium of equation (3) to the right and for the decrease in the rate of formation of pentathionate according to equation (4) [1, 7]. Pentathionate, at the low acidity of the medium, readily cleaves 1 atom of sulfur [5], and the tetrathionate formed in this manner is itself decomposed according to the equation

$$2S_4O_6'' \rightleftarrows S_5O_6'' + S_3O_6''. \tag{7}$$

The latter reaction is extremely accelerated catalytically by thiosulfate [8]. Therefore, it becomes understandable why the lower polythionates appeared in considerable amounts in these experiments even an hour after the start of the hydrolysis of sulfur dichloride.

Hydrolysis in hydrochloric acid. In the experiments described above on the hydrolysis of sulfur dichloride in pure water, all of the reactions proceeded, with the exception of the first moment of the hydrolysis, in acidic media but under conditions of a gradual increase in the concentration of hydrogen ions since the products of these reactions are strong acids - hydrochloric and pentathionic acid. In order to verify whether a large change in the concentration of free acid had a noticeable effect on the results of the reaction, sulfur dichloride was hydrolyzed, in subsequent experiments, in a large excess of 2 N hydrochloric acid (400 – 500 ml). Under these conditions the change of concentration of hydrogen ions during the reaction can be considered almost insignificant. Data of three experiments are given, in which the analysis of the reaction mixture was conducted at various periods of time after the start of hydrolysis (Table 3).

TABLE 3

Hydrolysis of Sulfur Dichloride in 2 N Hydrochloric Acid

Expt. No.	6		7		8	
Used:						
SCl_2 (in g)	5.338		6.287		6.810	
Hydrolysis time (in hrs)	2.5		3.5		12.	
Reaction products	Milli moles	% S	Milli moles	% S	Milli moles	% S
H_2SO_3	0	0	0.08	0.1	0.93	1.3
$H_2S_2O_3$	4.15	15.5	2.77	8.8	1.99	5.8
$H_2S_5O_6$	7.08	66.3	7.53	59.9	9.02	66.4
H_2S	Traces	0.0	0.63	1.0	0	0
H_2SO_4	5.30	9.9	7.17	11.4	2.37	3.5
S	6.46	12.1	10.87	17.3	15.72	23.0

The general picture here is almost the same as for the hydrolysis in pure water. Characteristically, here the main product is pentathionic acid; the lower polythionic acids are not found at all. The only essential difference, in comparison to hydrolysis in pure water, was the presence of considerable amounts of thiosulfuric acid. This must be explained by the fact that the stability of the latter, at large concentrations of the side acids, increases with increase of the concentration of hydrogen ions [9].

Hydrolysis in alkaline medium. Polythionates do not usually form in alkaline medium. But the hydrolysis of sulfur dichloride in alkaline solution was of interest because of the fact that here the formation of large amounts of thiosulfate could be expected This view results from the following considerations. According to the above hypothesis, pentathionate is formed in acidic medium not directly from hydrosulfurous acid, but through thiosulfuric acid. Therefore, reaction (3) must be of great importance during the hydrolysis of sulfur dichloride Hydrosulfurous acid is considered weak, while thiosulfuric acid is a strong acid: for this reason equilibrium (3) is shifted to the right with decrease of the concentration of the hydrogen ions. That the above is actually true is already shown by the results of the hydrolysis of sulfur dichloride in acetate buffer, where a considerable amount of thiosulfate is formed. If the above assumptions were correct, hydrolysis in alkaline medium should lead to the formation of still more thiosulfate This was verified completely by experimental results: in experiment 9 (Table 4) about 60% of sulfur taken in the form of SCl_2 was transformed into thiosulfate.

TABLE 4

Expt. No. 9. – Hydrolysis of 2.576 g SCl_2 in 150 ml 0.8 N NaOH

Hydrolysis time	1.5 hrs		10 days	
Reaction products	Millimoles	% S	Millimoles	% S
SO_3''	0.74	2.9	2.35	9.1
S_2O_3''	7.38	57.2	7.68	59.6
S_3O_6''	0.60	7.0	0	0
SO_4''	1.87	7.3	2.12	8.2
S	5.56	21.6	5.56	21 6

However, somewhat unexpected was the presence of a small amount of trithionate, because polythionates, as stated above, do not usually form in alkaline media. The formation of trithionate can be explained by the heterogeneous primary hydrolysis reaction of sulfur dichloride, since the latter is practically immiscible with water and aqueous solutions. A momentary appearance of a certain excess of hydrogen ions is possible as a result of reaction (2) in the boundary layer between the two liquid phases; i.e., conditions in which the formation of polythionates may occur. Since trithionate is the only polythionate which is capable of existing for any length of time in alkaline medium, its presence can be detected soon after the completion of the hydrolysis of sulfur dichloride. From the results it is also apparent that trithionate disappears with time, decomposing, as usual in alkaline medium, into thiosulfate and sulfite according to the equation:

$$2S_3O_6'' + 6OH' \rightarrow S_2O_3'' + 4SO_3'' + 3H_2O.$$

For the formation of trithionate by any method known up to now, the presence of ions of sulfuric acid is necessary [1,2]. In the above case, a more probable path for the formation of trithionate is the reaction of hydrosulfurous acid with bisulfite ions:

$$S(OH)_2 + 2HSO_3' \rightarrow S_3O_6'' + 2H_2O. \qquad (8)$$

But here a question arises in what manner is the sulfate formed during the hydrolysis, which upon first analysis is found in very small amounts. It can be supposed that the autoxidation reaction of hydrosulfurous acid (equation (6)) proceeds in two steps, of which the first leads to the formation of sulfurous acid:

$$2S(OH)_2 \rightarrow H_2SO_3 + S + H_2O. \qquad (9)$$

It is also possible that the last reaction is an independent side process which occurs simultaneously with the other transformations of hydrosulfurous acid under the given conditions of acidity.

The reaction leading to the formation of trithionate must, however, be evaluated as a side process during the hydrolysis of sulfur dichloride in alkaline medium, since the main product of the reaction is thiosulfate, formed as a result of the shift of equilibrium (3) to the right.

The following simple calculation may be given in favor of the authors' treatment of the hydrolysis of sulfur dichloride in alkaline medium. Elementary sulfur is formed as a result of the side reactions (6) and (9); namely, 2 g-atoms for 1 mole of sulfate formed, and 1 g-atom for 1 mole of sulfite. According to equation (8), 2 moles of sulfite are consumed for the formation of trithionate. Therefore, if the sulfite were formed according to equation (9) and were partially consumed for the formation of trithionate, then as many gram-atoms of sulfur must have separated as the moles of sulfite found plus double the number of moles of trithionate formed plus double the number of moles of sulfate found. According to the data of Table 4, the amount of elementary sulfur calculated in this manner is equal to:

$$0.74 + 2 \cdot 0.60 + 2 \cdot 1.87 = 5.68 \text{ milli-atoms},$$

while 5.56 milli-atoms of sulfur were found; i.e., an amount very close to the calculated.

In conclusion it must be mentioned that these experimental results on the hydrolysis of sulfur dichloride in alkali medium differ widely from the data of Goehring on the alkaline hydrolysis of ethyl hydrosulfite [2]. Goehring found approximately the same amount of thiosulfate and sulfite, and traces of sulfide, but no sulfur at all. Her results, however, arouse doubts, since they give no satisfactory sulfur balance. In addition, if there are considerable amounts of oxidation products of hydrosulfurous acid (for example, sulfite) among the reaction products, then they must be accompanied by equivalent amounts of reduction products, which Goehring, besides traces of sulfide, did not find. For this reason her conclusion that sulfite was a main product, in addition to thiosulfate, of the spontaneous decomposition of hydrosulfurous acid in alkaline mediun cannot be considered proved.

SUMMARY

1. The unstable hydrosulfurous acid formed during the hydrolysis of sulfur dichloride, is transformed into a mixture of products, the nature of which and relative amounts of which depend on the acidity of the medium.

2. By the hydrolysis of sulfur dichloride in pure water; i.e., under conditions of acidity which arise from the products of hydrolysis themselves, the main process is the transformation of hydrosulfurous acid into pentathionic acid.

3. Hydrolysis of sulfur dichloride in solutions of hydrochloric acid leads mainly to the same processes and products as hydrolysis in pure water.

4. Decrease of the concentration of hydrogen ions and its stabilization by acetate buffer lead to a partial stabilization of the thiosulfate formed; increase of the pH favors the secondary reactions leading to the formation of tetra- and trithionate.

5. In alkaline media the main reaction of hydrosulfurous acid is its transformation into thiosulfate.

6. A side reaction proceeds in all cases, in addition to the main one of hydrosulfurous acid given above, as a result of which elementary sulfur and sulfuric acid, or correspondingly, sulfate, are formed. This side reaction is evidently the auto-oxidation of hydrosulfurous acid.

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INVESTIGATION OF POLYTHIONIC ACIDS

III. FORMATION OF POLYTHIONIC ACIDS FROM SULFUR DICHLORIDE AND THIOSULFATE

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Even in 1870 D. I. Mendeleev believed that the structural formulas proposed by him for the polythionic acids could serve as starting points for the development of satisfactory methods for the preparation of these acids or their salts [1]. This soon stimulated the Belgian chemist, Spring, to attempt to synthesize trithionate and pentathionate by the action of sulfites and thiosulfates on sulfur dichloride. Spring actually obtained trithionate by shaking sulfur dichloride with a solution of potassium sulfite, but his attempts to obtain pentathionate by an analogous method; i.e., by using thiosulfate instead of sulfite, were unsuccessful [2].

The synthesis of pentathionate from sulfur dichloride and thiosulfate was only recently accomplished by Goehring and Feldman [3]. It is based on the reactions:

$$SCl_2 + 2H_2O \rightarrow S(OH)_2 + 2HCl, \quad (1)$$

$$S(OH)_2 + 2H_2S_2O_3 \rightarrow H_2S_5O_6 + 2H_2O. \quad (2)$$

The above authors, however, could not avoid side reactions during this synthesis, which proceeded to a considerable extent, as a result of which, under the conditions recommended by them, some elementary sulfur was formed. This is understandable since the formation of pentathionic acid, according to equation (2) requires a considerably acidic medium; i.e., not less than that in which the acid anions of the strong thiosulfuric acid [4] can be formed. The latter, as is known, is unstable and decomposes into sulfurous acid and sulfur, which leads, without taking into account the extreme instability of hydrosulfurous acid, to a series of side processes, and finally, to the side products of the synthesis.

In order to realize reaction (2) in such a way that it is least accompanied by side processes, it is necessary to introduce the hydrosulfurous acid at the moment of its formation; i.e., to hydrolyze sulfur dichloride in a solution of thiosulfuric acid in which the latter does not cleave sulfur. Two possibilities exist. The first is the use of thiosulfate in weakly acidic medium, as it cleaves sulfur only very slowly at pH > 3; the second is the use of freshly prepared Gil-Beato's solution containing essentially free thiosulfuric acid [5], as the medium for the hydrolysis of sulfur dichloride.

Both methods were tried with the first not leading to the desired results. For this reason, without going into detail, it can only be mentioned that the formation of pentathionate occurs according to equation (2) in weakly acidic medium (pH 3 to 5), although it is masked to a great extent by side processes. In addition to pentathionate, considerable amounts of tetrathionate and elementary sulfur, as well as small amounts of trithionate and sulfate, are formed. Evidently, the rate of reaction (2) is too slow under these conditions since the concentration of acidic thiosulfuric anions, or the free acid, does not acquire a noticeable value under the given acidity of the medium. Because of this fact, the primary hydrolysis product of sulfur dichloride, hydrosulfurous acid, is not able to react quantitatively with thiosulfate, and partially decomposes in different directions, apparently, as it does in the absence of thiosulfate [6].

Because reaction (2) is related to the consumption of hydrogen ions, a considerable increase in its rate could be expected by the use of thiosulfuric acid in a sufficiently acidic medium, which is Gil-Beato's solution. This view, as will be shown below, was completely proved. In addition, the study of the action of this solution on sulfur dichloride led to a new method for the preparation of solutions of polythionic acids; i.e., six and more atoms of sulfur in the molecule.

EXPERIMENTAL

150 ml of concentrated hydrochloric acid (d 1.175) was cooled to −20°; a weighed amount of thiosulfate, initially dissolved in a small amount of water, was added with gentle shaking to the cold acid. Only sodium chloride precipitated. An ampoule containing an accurately weighed amount of sulfur dichloride was introduced into the Gil-Beato solution obtained in this manner, the bottle was tightly stoppered, and the ampoule was broken by shaking. At the end of the hydrolysis (disappearance of SCl_2), the solution obtained was transferred into a volumetric

flask and diluted to 200 ml with concentrated hydrochloric acid. The solution was stored at 0°. The analysis was conducted by a method, developed by one of the authors, for Gil-Beato's solution, and which made possible the determination of thiosulfuric acid, the number of moles of polythionic acid, average number of sulfur molecules in the latter (n), and the sum $SO_2 + H_2S$ [5]. This sum could be practically considered as sulfurous acid, since hydrogen sulfide appeared only in traces. Elementary sulfur did not form at all during the hydrolysis of sulfur dichloride in Gil-Beato's solution.

TABLE 1

Hydrolysis of Sulfur Dichloride in Gil-Beato's Solution

Expt. No.	1		2		3	
Used (milli-moles):						
SCl_2	9.34		8.65		11.44	
$Na_2S_2O_3$	15.41		19.32		27.75	
Time of analysis* (in min)	60		30		30	
Reaction products	Milli-moles	% S**	Milli-moles	% S**	Milli-moles	% S
$H_2S_2O_3$	0.10	0.5	1.85	7.8	4.72	14.1
SO_2	2.07	5.1	1.55	3.3	2.10	3.1
$H_2S_nO_6$	7.27	91.6	8.86	93.7	11.52	87.3
n	5.06		5.0		5.08	
Consumption $H_2S_2O_3$: $H_2S_nO_6$ found	2.1:1		1.97:1		2.0:1	

Table 1 gives the results of several experiments in which 1.65 to 2.4 moles of thiosulfate were used for 1 mole of sulfur dichloride. The analysis of the mixture was conducted almost immediately after the disappearance of the sulfur dichloride.

It is apparent from the results given that the main reaction product is pentathionic acid, in which form 90% and more of the sulfur used is found. The ratio of the number of molecules of reacted thiosulfate to the number of molecules of polythionic acids formed was close to 2:1 in all cases as required by the equation:

$$S(OH)_2 + 2H_2S_2O_3 \rightarrow H_2S_5O_6 + 2H_2O. \qquad (2)$$

In experiments 2 and 3, the number of millimoles of pentathionic acid found is also close to the number of millimoles of sulfur dichloride used The deviation from these results in experiment 1 is explained by the fact that some excess sulfur dichloride was used here, as a result of which part of the hydrosulfurous acid was converted into pentathionic acid in the same manner as with the hydrolysis in the absence of thiosulfate [6]; i.e., according to the general equation:

$$5S(OH)_2 \rightarrow H_2S_5O_6 + 4H_2O. \qquad (3)$$

This explanation was confirmed by the fact that the starting thiosulfate reacted almost completely in experiment 1, whereas in both of the other experiments, in which a small excess of thiosulfate based on the ratio $SCl_2 : Na_2S_2O_3 = 1:2$ was used, this excess remained unused.

Therefore, it follows from these experimental results that the hydrolysis of sulfur dichloride in Gil-Beato's solution leads to practically a quantitative formation of pentathionic acid according to equation (2).

A phenomenon, which appeared strange at first, was observed upon repeating these experiments. It was frequently found that the number of moles of polythionic acid formed was considerably less than the starting number of moles of sulfur dichloride, but the average number of sulfur atoms in the molecules of these acids (n) was found to be much higher than five in these cases. Therefore, in such experiments, in addition to pentathionic acid, hexathionic and other higher polythionic acids must have been formed. Table 2 gives the results of two such experiments with "anomalous" results.

The fact must be kept in mind that the consumption of thiosulfuric acid for 1 mole of polythionic acid is considerably greater than 2 moles in these experiments. This fact leads to the conclusion that hexathionic acid is formed as a result of the secondary reaction:

$$H_2S_5O_6 + H_2S_2O_3 \rightleftarrows H_2S_6O_6 + SO_2 + H_2O. \qquad (4)$$

---

* From the start of the sulfur dichloride hydrolysis.

** The sulfur used is taken as 100%.

TABLE 2

"Anomalous" Results of the Hydrolysis of Sulfur Dichloride in Gil-Beato's Solution

Expt. No.	4		5	
Used (millimoles):				
SCl_2	8.76		11.43	
$Na_2S_2O_3$	17.0		24.42	
Time of analysis (in hrs)	2		1	
Reaction products	Milli-moles	% S	Milli-moles	% S
$H_2S_2O_3$	2.61	12.8	2.65	9.1
SO_2	3.63	8.9	3.21	5.5
$H_2S_nO_6$	5.58	78.1	8.68	83.7
n	5.7		5.6	
Consumption $H_2S_2O_3$: $H_2S_nO_6$ found	2.58:1		2.51:1	

The great difference between the "anomalous" results of these experiments and the results of experiments 1 – 3 is explained by the heterogeneous process of the hydrolysis of sulfur dichloride. Sulfur dichloride is not miscible with aqueous solutions, and the formation of hydrosulfurous acid occurs on the interfacial surface between the liquid phases. For this reason its rate of formation depends upon factors very difficult to control, like the rate of mixing and the size of the interfacial surface between the phases. Since hydrosulfurous acid reacts extremely rapidly under these conditions, which is shown by the fact that almost no auto decomposition occurs, which is usually accompanied by the precipitation of sulfur [1], the rate of formation of pentathionic acid according to (2) must depend mainly upon the rate of the heterogeneous process of hydrolysis of sulfur dichloride. It can be supposed that, for example, with an insufficiently efficient shaking of the reaction mixture, the formation of hydrosulfurous acid does not occur with sufficient speed, and the thiosulfuric acid found in the solution is practically consumed for the sulfuration of the pentathionic acid already formed according to (4), instead of according to equation (2) for the formation of pentathionic acid.

In order to prove this explanation for the formation of hexathionic acid; i.e., reality of reaction (4), the change of the composition of the reaction mixture with time was determined in the subsequent experiments. In experiment 6 (Table 3), analyses conducted a half hour after the start of the hydrolysis of sulfur dichloride showed a "normal" composition of reaction products; i.e., analogous to those obtained in experiments 1 – 3. Analysis conducted after 2.5 to 5 hours showed that polythionate sulfur and the average number of sulfur atoms in the polythionic acid molecules (n) increased with time because of the remaining thiosulfuric acid. Therefore the existence of the secondary sulfuration reaction of pentathionic acid according to equation (4) cannot be disputed.*

TABLE 3

Expt. No. 6. Change of the Composition of the Hydrolysis Products of 9.33 Millimoles of SCl_2 in a Gil-Beato's Solution Prepared from 22.65 Millimoles of $Na_2S_2O_3$

Time from beginning of hydrolysis	30 minutes	2.5 hours	5 hours
% S in form of $H_2S_nO_6$	89.4	91.9	93.6
n	5.05	5.08	5.12
% S in form of $H_2S_2O_3$	10.4	9.6	7.2

The results led to the idea of using the hydrolysis of sulfur dichloride in a Gil-Beato's solution for the preparation of hexathionic acid. Since the latter is formed by means of the reversible reaction (4), an excess of thiosulfuric acid must shift this equilibrium to the right. For this reason, in subsequent experiments, the starting ratio of thiosulfate: sulfur dichloride was changed to 3:1 and 4:1 (experiments 7 and 8, Table 4).

In both experiments, the analysis was initially conducted at practically the end of the hydrolysis of sulfur dichloride, and then several hours later. The results in Table 4, as well as their comparison with those of previous experiments (for example, 2, 3, and 6), show that the average number of sulfur atoms in the polythionic acid molecule (n) is higher, the greater the excess of thiosulfate used based on the ratio $Na_2S_2O_3$: SCl_2 = 2:1. This number also increases considerably with time which is accompanied by the consumption of thiosulfuric acid and an increase in the amount of sulfur dioxide in the solution. Therefore, these experiments also prove that the formation of the higher polythionic acid occurs according to equation (4).

The use of 3 moles of thiosulfate for 1 mole of sulfur dichloride (experiment 7) gives a solution whose analysis after 3.5 hours at 0° reveals that hexathionic acid with a small impurity of unreacted thiosulfuric acid and sulfur dioxide was present.

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* The possibility of the formation of hexathionate from pentathionate according to equation (4) has been questioned by several authors [7].

TABLE 4

Hydrolysis of Sulfur Dichloride in the Presence of Thiosulfuric Acid

Expt. No.	7				8			
Used (m-moles)								
SCl_2	10.36				13.38			
$Na_2S_2O_3$	30.18				52.0			
Time of analysis	30 minutes		3.5 hours		30 minutes		2 hours	
Reaction products	Millimoles	% S	Millimoles	% S	Millimoles	% S	Millimoles	% S
$H_2S_2O_3$	5.64	15.9	4.97	14.0	8.27	14.2	6.81	11.7
SO_2	5.61	7.9	6.83	9.6	17.69	15.1	20.0	17.1
$H_2S_nO_6$	9.25	74.0	8.80	74.2	13.77	72.3	13.34	72.0
n	5.68		5.99		6.13		6.3	

Increasing this ratio to 4:1 (experiment 8), results in a solution of practically analogous composition at once; i.e., during the first analysis, which was conducted a half hour after the start of hydrolysis. Two hours later, a considerable amount of heptathionic acid, and possibly other acids with $n > 6$ were present.

The formation of higher polythionic acids; i.e., with $n \geq 6$, from sulfur dichloride and thiosulfate has been unreported in the literature up to now.

The authors were not satisfied with the analysis of the solution obtained, which showed the presence of higher polythionic acids, and made a series of attempts to obtain these acids as benzidine salts. The procedure used was analogous to that reported in one of the previous communications. The precipitates obtained by the addition of a benzidine hydrochloride solution to the reaction mixture were usually recrystallized from 1N hydrochloric acid and dried at room temperature in a desiccator. A short characterization of the preparations obtained is given in Table 5.

TABLE 5

Analysis of Benzidine Polythionates

Preparation No.	% S, found	% S, calculated according to the formula	Notes
1	43.8		Used $Na_2S_2O_3 : SCl_2 = 3.9:1$
		44.3 Bz $H_2S_7O_6$*	Fraction I precipitate, recrystallized
2	44.2		$Na_2S_2O_3 : SCl_2 \approx 3:1$;
			Fraction I recrystallized
3	50.0	50.5 Bz $H_2S_9O_6$	" " not recrystallized
4	45.8	47.5 Bz $H_2S_8O_6$	" " recrystallized
5	37.6		Fraction II, after removal of preparation 4; recrystallized.
		36.3 Bz $H_2S_5O_6$	
6	37.3		Fraction II, recrystallized.

The analytical results show that Fraction I of the precipitate formed by benzidine, contains polythionates with 7 – 9 sulfur atoms in the molecule; pentathionate predominates in Fraction II. The composition of preparation No. 2 very nearly corresponds to the formula for the heptathionate; preparation No. 3 is close to nonathionate. However, sufficient basis was not found for considering these preparations to correspond to individual compounds; rather there is an inclination to regard them as mixtures, because they could not be reproduced.

However, these experiments do not leave any doubt that higher polythionic acids are formed upon the hydrolysis of sulfur dichloride in Gil-Beato's solution containing an excess of thiosulfuric acid. Their formation can be expressed, considering the presence of acids with $n > 6$ in the solutions, by the general equation:

$$H_2S_5O_6 + (n-5)H_2S_2O_3 \rightleftarrows H_2S_nO_6 + (n-5)H_2SO_3. \qquad (5)$$

In addition the redistribution reaction of sulfur between the molecules of polythionic acids [8] is very probable; for example, according to the equation:

$$2H_2S_6O_6 \rightleftarrows H_2S_7O_6 + H_2S_5O_6. \qquad (6)$$

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* Bz = $C_{12}H_8(NH_2)_2$

SUMMARY

1. Hydrolysis of sulfur dichloride in Gil-Beato's solution led very rapidly and practically quantitatively to the reaction of hydrosulfurous acid with thiosulfuric acid according to the equation:

$$S(OH)_2 + 2H_2S_2O_3 \rightarrow H_2S_5O_6 + 2H_2O \qquad (2)$$

2. The use of an excess of thiosulfate based on the ratio $Na_2S_2O_3 : SCl_2 = 2:1$ made possible the formation of higher polythionic acid solutions under these conditions. These acids were formed from pentathionic acid as a result of the reaction:

$$H_2S_5O_6 + (n-5)H_2S_2O_3 \rightleftarrows H_2S_nO_6 + (n-5)H_2SO_3. \qquad (5)$$

3. Benzidine polythionates were obtained whose composition varied between heptathionate and nonathionate.

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* See Consultants Bureau Translation, page 1509.

INVESTIGATION OF THE SYSTEM PLATINUM-OXYGEN

II. ENTHALPY OF FORMATION OF PLATINIC OXIDE Pt_3O_4

S. M. Ariya, M. P. Morozova, and A. A. Reikhardt

Establishment of the homogeneity of the product of the oxidation of platinum with oxygen made possible the start of the study of the thermodynamics of this compound. The reaction of platinic oxide with hydrogen was chosen in order to establish the enthalpy of its formation.*

$$[Pt_3O_4] + 4(H_2) \rightarrow 4H_2O + 3[Pt].$$

This reaction starts the moment of contact between hydrogen and platinic oxide at room temperature; it does not require any catalysis and proceeds rapidly. Platinum is obtained in the form of grey powder, i.e., with small specific surface, which excludes any possibility of distorting the value of the thermal effect because of the heat of adsorption of the hydrogen on the surface of the metal. The completeness of the reduction of the oxide under these conditions was established experimentally. Therefore, the reduction reaction of Pt_3O_4 with hydrogen satisfies the requirements of reactions that are to be effected in a calorimeter.

The calorimetric vessel was a brass cylinder with a ground brass cover. A heater (a copper ring wound with constantan wire) was placed in the center within the cylinder. A glass ampoule containing a sample of the preparation (0.25g-0.45g) weighed on an analytical balance with an accuracy of 0.2 mg, from which the air was removed until a residual pressure of 10^{-4} mm, was suspended after sealing, from the cover of the vessel with tungsten threads. The calorimetric vessel was hermetically sealed and evacuated through a small vacuum stopcock placed in the cover of the vessel to the above residual pressure. The hydrogen, completely purified from oxygen, was introduced into the calorimetric vessel with sufficient moisture in it to saturate it with water vapor. The center of the cover had a cavity in which a thermal resistor was placed.

The calorimetric vessel was suspended, insulated by the cover, in a sheath which was a hollow brass cylinder hermetically sealed with a cover to which tubes were connected for the exit of wires going to the thermal resistor, heater, and tungsten threads. A second auxiliary brass vessel was placed in this envelope, which served to decrease the heat exchange between the calorimetric vessel and its surroundings.

The hermetically sealed envelope was placed in about a 100-liter water thermostat in which were installed two stirrers, a heater, and thermoregulator by means of which, with the aid of a vacuum tube relay, the temperature of the thermostat was held at 25 ± 0.01°. The resistance of the thermal resistor was measured with a Wheatstone bridge (Etalon). A Siemens mirror galvanometer was used as the zero instrument. Upon using a subjective method, the reading could be made to an accuracy of 0.1 ohm. A change in the temperature of 1° corresponded to a change of the resistance of 209 ohms, i.e., 0.1 ohm corresponded to a change of temperature of 0.0005°. The strength of the current in the thermal resistor was only of the order of 0.0004 A, which made it possible to neglect the energy separating from it.

Before the start of each series of experiments, the presence of a linear relationship between the uncompensated bridge and the deviation of the mirror of the galvanometer was determined. When the calorimetric vessel attained a temperature of 24.5°, a measurement of the resistance of the thermal resistor was conducted in 30-second intervals. If the changes of the resistance were equal during 12-15 measurements, then the tungsten wire on which the ampoule with the preparation hung, was melted. Falling, the ampoule was broken on the bottom of the vessel, and the preparation reacted with the hydrogen.

The increase of the temperature at the time of the experiment with the platinic oxide was compared with the increase of the temperature which occurred when energy was introduced into the calorimetric vessel by the passage of a current across the heater. The fall of the resistance on ends of the heater was measured potentiometrically. The correction for the heat exchange of the calorimetric vessel with the surroundings was introduced by the Reniot-Pfaundler equation [2]. The correction was from 1.5-4%.

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* The same reaction, reduction of the oxide, was used by Wöhler [1] for the determination of the enthalpy of formation of PdO.

On the basis of the above reported measurements of the enthalpy of the reaction

$$[PtO_{1.39}] + 1.39(H_2) = [Pt] + 1.39H_2O$$

the enthalpy of formation of the oxide of this composition was found to be equal in a series of experiments, to: -14.7, -13.0, -12.9, -13.8, -14.0, and 13.3 kcal. Therefore, -13.6 ± 1.1 kcal. is obtained as an average for the enthalpy of formation of

$$[Pt] + 0.695(O_2) \rightarrow [PtO_{1.39}] + 13.6 \pm 1.1 \text{ kcal}$$

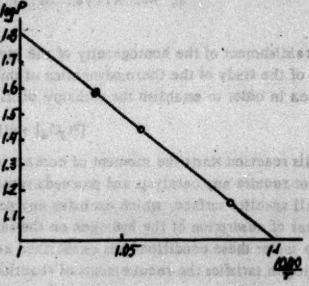
The temperature relation of the value of the oxygen pressure, corresponding to the equilibrium

$$[PtO_{1.33}] \rightleftarrows [Pt] + 0.665(O_2).$$

was investigated.

The values obtained are given in the Table.

Temperature	Equilibrium pressure of oxygen (in kg/cm$_2$)
650°	14.2
680°	27.6
700	37



The Figure gives the relation of the logarithm of the dissociation elasticity of platinum oxide to the inverse value of the absolute temperature. All three points, as the Figure shows, satisfactorily fit on a straight line.

Considering the change of enthalpy and entropy of this process approximately constant at 650-700°. It is found (using the generally known thermodynamic equation RT ln K = ΔH − TΔS) correspondingly,

$$\Delta H_{675°C} = 11.5 \text{ kcal and } \Delta S_{675°C} = 43.1 \text{ kcal/1°}$$

The enthalpy of formation of the oxide at room temperature must be somewhat higher (in absolute value), i.e., the value found by tensiometric results confirms that obtained calorimetrically.

The enthalpy of formation of nickel and palladium oxides, analogs of platinum in the vertical column of the periodic system, are higher in absolute value, namely for NiO = − 58.4 kcal, for PdO = −20.4 kcal.

Nickelous oxide has considerably different properties from palladium and platinum oxides which can be assigned to the metal-like oxides (they possess, for example, in contrast to NiO, a high metallic electroconductivity), while nickelous oxide resembles the salt-like oxides. It is natural, for this reason, to compare the values of the enthalpy of formation of PdO and $PtO_{1.39}$.

Previously it was stated that an oxide, close in composition to the formula Pt_3O_4 is the only thermodynamically stable phase in the system platinum-oxygen*. In other words, the process of disproportionation of the hypothetical oxide PtO

$$[PtO] \rightarrow 0.72[PtO_{1.39}] + 0.28[Pt]$$

must be accompanied by a decrease of free energy. Since only solid phases participate, the change of entropy can be neglected, and with a good degree of accuracy, it can be considered that PtO disproportionates because of the exothermic nature of the above-given reaction. In other words, the heat of formation of PtO must be less than +9.8 kcal/mole (the heat of formation of 0.72 $PtO_{1.39}$). In addition, this value, in all probability, is greater than zero, i.e., it can be supposed that it is confined to the interval 0-10 kcal.

If the enthalpies of formation of PdO and PtO are calculated from oxygen in its standard state and from monoatomic vapors of the metals (enthalpy of vaporization of Pd is 110 kcal., Pt, 127 kcal [4], the following values are obtained:

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* Recently [3] a paper by Galloni and Busch appeared in which the authors also came to the conclusion that the existence of PtO reported by a series of authors, must be doubted.

$$(Pt) + 1/2(O_2) \rightarrow [PtO] + 127 - 137 \text{ kcal.}$$

$$(Pd) + 1/2(O_2) \rightarrow [PdO] + 130 \text{ kcal.}$$

If it is considered that the enthalpy of vaporization of the above metals, actually, is determined without sufficient accuracy, both values may be considered practically equal, i.e., in other words, the decrease of stability of oxides upon going from palladium to platinum is mainly due to the increase of stability of the metallic lattice in this direction.

SUMMARY

1. The enthalpy of the reaction

$$[PtO_{1.39}] + 1.39(H_2) = [Pt] + 1.39H_2O$$

was determined calorimetrically; the value of the enthalpy of formation of platinic oxide was found to be:

$$\Delta H_{\text{formation}}\, PtO_{1.39} = -13.6 \pm 1.1 \text{ kcal.}$$

2. The above value agrees with the results of the investigation of the equilibrium of the process of dissociation of platinic oxide.

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TERNARY COMPLEXES IN THE SYSTEM COPPER IONS-PYRIDINE-SALICYLATE

II. RELATION OF THE COMPOSITION OF THE COMPLEXES TO THE pH OF THE SOLUTION

A. K. Babko and M. M. Tananaiko

During the reaction of cuprous ions with pyridine and salicylic acid, the formation of poorly soluble complex compounds occurs, which are readily extractable by non-aqueous solvents. Chloroformic extracts of the complex are colored intense blue, and for this reason, the reaction is used for the colorimetric determination of copper [1] and salicylic acid [2].

There is data in the literature on pyridine salicylate complexes of the composition $CuPy_2Sal_2$ [3], as well as $CuPy_2Sal_2$ $2CuPy_2Sal$; $2CuPy_2Sal_2 \cdot CuPy_2Sal$ [4]. These complexes were isolated in solid form by mixing solutions of the corresponding amounts of the starting substances. Any relationship of the equilibrium in aqueous solution to the pH of the solution, etc., was not established by these authors; the question of the structure of these complexes also were not discussed.

In 1948, one of the authors of the present communication [5] studied the complex formation in the system copper ions-pyridine. A method for the physico-chemical analysis of a system with three reaction components in solution was developed. The results of the investigation showed the formation of the ternary complex $CuPy_2Sal$, in the system, stable at known limits of concentration, in which the copper is coordinately attached to the pyridine and salicylate ion. Later, the equilibrium between the reaction components in the above system was studied [6].

A more detailed investigation, the results of which are reported in the present communication, led to the conclusion that the reaction of copper with pyridine and salicylate resulted in the formation of several ternary compounds of various composition.

Salicylic acid, which enters into the composition of the copper pyridine salicylate complex, is a weak acid. Its degree of dissociation, and correspondingly, participation in complex formation to a considerable extent depend on the acidity of the solution. For this reason, complex formation in the system copper ion-pyridine-salicylate was studied in relation to the pH of the medium. The investigation was conducted on the basis of the change of the optical characteristics of the solutions. Since the copper pyridine-salicylate complexes were readily soluble in non-aqueous solvents, chloroformic extracts, as well as aqueous solutions were studied.

Spectral Characteristics of the Solutions

Absorption spectra of the copper pyridine-salicylate complex were studied at various pH's. The optical densities of aqueous solutions and chloroformic extracts were measured. The measurements of the light absorption values of the extracts directly characterized the ternary complex, since the secondary copper complex with pyridine, as well as copper with salicylic acid, was not extractable with non-aqueous solvents [5].

The acidity of the medium was changed by the addition of 0.1 N sodium hydroxide or 0.1 N nitric acid*. To conduct this experiment, 2 ml of 0.05 M copper nitrate solution, 4 ml of 0.05 M pyridine, and 4 ml of 0.05 M sodium salicylate were mixed together in test tubes. After mixing, acid or base was added to the solution. The solutions were mixed, and their optical densities were measured on the FM photometer.

Another series of analogously prepared solutions was shaken with 5 ml of chloroform, and the light absorption of the obtained extracts was measured. Parallelly, the pH was measured with a vacuum tube potentiometer of the LP-4 type with quinhydrone electrodes. The absorption spectra obtained as a result of the investigation are given in Figs. 1 and 2.

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* Buffer solutions were not used since the substances entering into their composition could have affected the complex formation.

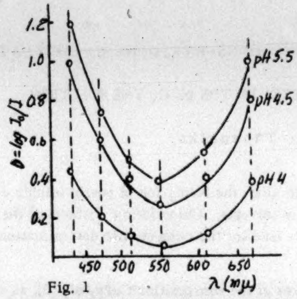


Fig. 1

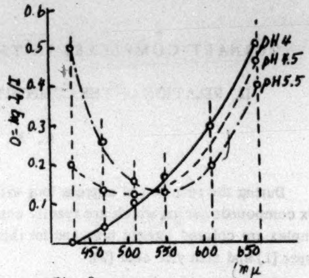


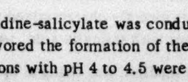
Fig. 2

As it is apparent (Fig. 1) in aqueous solutions, increase of pH does not affect the character of the light absorption of the solutions, but only results in the increase of the optical density. All of the solutions were green in color, and intensely absorbed in the red and violet parts of the spectrum. A formation of a precipitate occurs at pH $>$ 6.

The more characteristic absorption spectra of the chloroformic extracts is given in Fig. 2. In this case, some decrease of light absorption in the red and a strong increase in the violet parts of the spectrum occur upon increasing the pH of the aqueous phase. Correspondingly, the color of the extracts goes from blue to yellow.

At pH of 4 to 4.5 in the aqueous phase, a blue colored compound is extracted. At pH of 5 to 5.5, the color of the extracts becomes green. At pH $>$6 the amount of the substance extracted decreases without change of the character of light absorption.

On the basis of the results obtained, it may be concluded that the reaction of copper with pyridine and sodium salicylate leads to the formation of two ternary complexes having the same color in the aqueous phase, but different colors in non-aqueous solvents. In more acidic media, (pH 4-4.5), a blue colored compound is formed; at pH 5-5.5, the formation of a complex having a green color in chloroform occurs.

Further increase of pH (pH $>$ 6), as it was shown previously [6], leads to the disruption of the ternary, and the formation of the more stable copper disalicylate complex  $\left[Cu\left(\begin{matrix}O\\OOC\end{matrix}>C_6H_4\right)_2\right]^{-2}$, which is not extractable with non-aqueous solvents.

Physico-Chemical Analysis of the Solutions

The physico-chemical analysis of the system copper-pyridine-salicylate was conducted with two series of solutions. In the first series, conditions were created which favored the formation of the complex having a blue color in the non-aqueous phase. For this reason, starting solutions with pH 4 to 4.5 were prepared. In the second series, alkali was added to pH~5.5 to analogous solutions in order to obtain compounds which extracted green. 0.05 M solutions of copper nitrate, pyridine, and sodium salicylate were used for the investigation. The solutions were mixed at various ratios, but in such a manner that the volume of all three components was always constant and equal to 10 ml.

Thus, for example, solutions corresponding to points 1-10 on the triangle diagram in Fig. 3, were prepared by the mixing of 1, 2, 4 . . . . . 10 ml of 0.05 M $Cu(NO_3)_2$ with 9, 8, 6 . . . . . 0 ml of 0.05 M pyridine. Solutions, corresponding to points lying within the triangle diagram, were prepared by mixing all three components. For example, the solution, corresponding to point 36, was prepared by mixing 2 ml of 0.05 M copper nitrate, 4 ml 0.05 M, pyridine, and 4 ml of 0.05 M sodium salicylate.

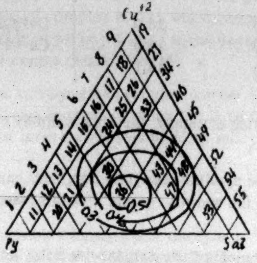


Fig. 3.

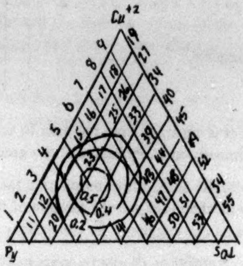


Fig. 4.

The measurements of the light absorption of the aqueous solutions were conducted with two light filters having an effective wavelength of 670 and 430 mμ respectively. Judging by the data in Figs. 1 and 2, the most characteristic results could be expected in these parts of the spectrum. The optical density of solutions of the ternary complex in chloroform was studied in supplementary experiments for each series. 10 ml of the aqueous solution was shaken with 5 ml of chloroform, and the optical density of the extracts obtained was measured. The method for processing the results remained the same as in the previous communication [5]: binary diagrams were constructed on the basis of the values of the absorption found, which were sections through the triangle diagram (Fig. 3) with lines parallel to the side Cu-Py. Points on Fig. 3 corresponding to compositions having identical absorption values, were sought from the data of the binary diagrams. Isochromes were obtained by joining these points with lines.

Fig. 3 gives the isochromes obtained by measurement of the optical density of chloroformic extracts at pH 4-4.5 in the aqueous phase. From the form of the isochromes, it can be concluded that the maximum optical density corresponds to a ratio of Cu : Py : Sal = 1 : 2 : 2.

In the second series of experiments, measurements were conducted analogously but with this difference: sodium hydroxide was added to the solutions until the transition of the color of the chloroformic extract from blue to green. It was found empirically that 2 ml of 0.1 N alkali was sufficient under the above reported conditions. As shown experimentally, the pH of the solutions was about 5.5. Fig. 4 gives the isochromes obtained by measuring the optical density of green chloroformic extracts. As it is apparent from the data of this figure, the maximum absorption corresponds to a ratio of Cu : Py : Sal = 1 : 2 : 1. Analogous results were obtained by the measurement of the optical density of aqueous solutions.

Therefore, physico-chemical analysis of the system led to the conclusion that the complex $CuPy_2Sal_2$ was formed at pH 4.5. At pH 5.5, the formation of the complex $CuPy_2Sal$ occurs.

Because the above complexes were sufficiently poorly soluble in water, they were isolated in the solid phase. Precipitates were obtained by the treatment of 10 ml of a 0.1 M solution of copper nitrate with a mixture of 10 ml 1 M sodium salicylate and 10 ml 1 M pyridine at various acidity. The treatment of a copper nitrate solution with the precipitating mixture with the addition of 0.5 ml of 0.1 N nitric acid led to the formation of a white powdery residue. If 1 ml of 0.1 N sodium hydroxide was initially added to the precipitant, a green flocculant precipitate of copper pyridine salicylate formed. The residues were filtered, washed with cold water, and dried at room temperature between sheets of filter paper.

It was shown experimentally that the blue residue dissolved in chloroform with the formation of a blue solution. The green residue gave a green chloroformic extract.

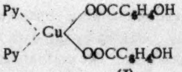
In order to confirm the composition of the complexes, the copper content was determined in the preparation obtained. The copper was analyzed electrolytically. The analytical results are given in the Table.

	Sample (g)	Cu found (g)	Cu found (%)	Cu calculated (%)
Blue complex	0.20	0.0262	13.1	$CuPy_2Sal_2$
	0.50	0.0628	12.1	Cu – 12.82
Green complex.	0.10	0.0180	18.0	$CuPy_2Sal$
	0.15	0.0270	18.0	Cu – 17.78
	0.20	0.0362	18.1	

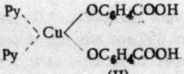
As it is apparent from the data in the Table on the determination of copper, the blue complex corresponds to the composition $CuPy_2Sal_2$, and the green – $CuPy_2Sal$.

Salicylic acid, which enters into the composition of the copper pyridine-salicylate complex, can dissociate with the cleavage of hydrogen of the carboxylic group, or of the hydroxyl group. For this reason, several structures can be suggested for the ternary complexes formed.

Structures (I or II) can be suggested for the structure of blue complex $CuPy_2Sal_2$ in which the copper substitutes the carboxylic hydrogen, or that of the hydroxyl group of the acid:



(I)



(II)

Upon the increase of the pH, the substitution of the other hydrogen atoms (hydroxylic or carboxylic groups of salicylic acid) is facilitated, and the formation of a "chelated" compound (III) * can occur

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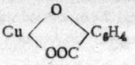
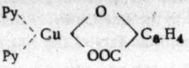


(III)



(IV)

which reacting with pyridine, forms the green complex (IV).

To solve the problem of the structure of the ternary complexes, supplementary experiments on the investigation of the extractability of the copper complexes with pyridine and methyl salicylate, as well as of the first two compounds with methoxybenzoic acid, were conducted.

It was shown experimentally that compounds were formed by the reaction of copper with pyridine and methoxybenzoic acid, which gave blue chloroformic extracts. The complex with pyridine and methyl salicylate was extracted with the formation of a green extract. Acidification of the solutions led to the decomposition of the complexes and the decolorization of the non-aqueous phase. Upon making the solutions alkaline, the blue complex was decomposed, while the green remained stable even in 1 M alkali solutions.**

From the results obtained, it could be concluded that the copper is bound to the carboxylic group of salicylic acid in the blue complex $CuPy_2Sal_2$ (Structure I), since the formation of a compound giving a green chloroformic extract could be expected with the presence of a bond across the hydroxyl group. The formation of green extracts by the complex $CuPy_2Sal$, without doubt, can be explained by the presence of a bond of copper with the OH group of salicylic acid in this compound in addition to that with the carboxylic group.

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* Another suggestion for the complex $CuPy_2Sal$, apparently cannot be made, since, if copper substituted only one of the hydrogen atoms in salicylic acid, the formation of (at a ratio of Cu : Sal = 1:1) a single charged cation would have occurred, which could not be extracted, since it cannot form a neutral molecule with the PyH^+ pyridine cation, as well as form a molecule with molecular pyridine.

** The stability of the complex of copper with pyridine and methyl salicylate is aided, evidently, by the absence of possibility for transition to copper disalicylate $[CuSal_2]^{-2}$, which occurs for the corresponding complex of copper with salicylic acid.

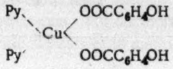
Therefore, the investigation of the optical characteristics of the solutions, analysis of the solid substances, and the study of the extractability of complexes of copper with pyridine and certain derivatives of salicylic acid, lead to the conclusion that the reaction of copper with pyridine and salicylic acid leads to the formation of several compounds. Complex (I), in which the copper is bound to the carboxylic group of the acid, is formed in more acidic solutions which hinder the dissociation of the hydroxyl group. By increasing the pH, the substitution of the OH group hydrogen of salicylic acid is facilitated, which leads to the formation of complex (IV), in which copper is bound to the carboxylic and the hydroxyl groups of the acid. Increase of pH to >6 leads to the decomposition of the ternary complexes, and the formation of the more stable copper disalicylate [4].

Of the two pyridine-salicylate copper complexes, the blue one, $CuPy_2Sal_2$, is more soluble in nonaqueous solvents, because of which it can be successfully applied for the separation of copper from cations which do not form extractable pyridine salicylate complexes.

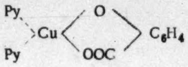
SUMMARY

The complex formation in the system copper ion–pyridine–salicylate was studied in relation to the acidity of the solution. Methods of physico-chemical analysis of colored ternary complexes in solution were used for the investigation. The optical density of the aqueous solutions, as well as the absorption of the chloroformic extracts, were the properties measured.

It was found that at pH of the aqueous phase from 4 to 4.5, ternary complex (I) was formed; while at pH 5 – 5.5 the formation of complex (IV) occurred:



(I)



(IV)

The data on the composition of the complexes were confirmed by the isolation of solid compounds, as well as the study of certain derivatives.

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OXIDATION OF ALCOHOLS BY THE EFFECT OF ULTRASONIC FREQUENCIES

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It is known that ultrasound causes oxidation reactions in pure water and in aqueous solutions [1-5]. The decomposition of starch, inulin, agar-agar, as well as intense chemical changes in the monomers – glucose, fructose, galactose, and maltose, are caused by sound, accompanied by the formation of acids and aldehydes [6, 7].

The action of ultrasonic frequencies leads to the decomposition of polypeptide chains and formation of ammonia and aldehydes in solutions of gelatin [8]. Amino acids are also subject to chemical change by this treatment. The available data indicates that cavitations formed by the action of ultrasonic vibrations cause the activation of oxygen, dissolved in the liquid, and the decomposition of water with the formation of free radicals and hydrogen peroxide [9, 10]. It was shown that the effect of ultrasonic vibration was similar to the action of ionizing radiation [11].

Because of the study undertaken on the effect of ultrasound on chemical processes [6-8, 12], it appeared of great interest to elucidate more fully the character of the oxidation reactions occurring under the influence of ultrasonic vibrations. For this reason, aqueous solutions of methyl alcohol and other alcohols, as well as various organic substances in methyl alcohol were subjected to sonation.

A high frequency oscillator described in previously published investigations [8], served for the preparation of ultrasonic vibrations. The strength of the oscillatory circuit was about 300-400 volts. The diameter of the prezog quartz plate was 50 mm. The frequency was 300 k-hertz/sec. The temperature of the solutions did not rise over 40° during the time of sonation. The solutions subjected to the action of ultrasound were placed, in 25 ml amounts, into conical vessels closed with stoppers during the experiment.

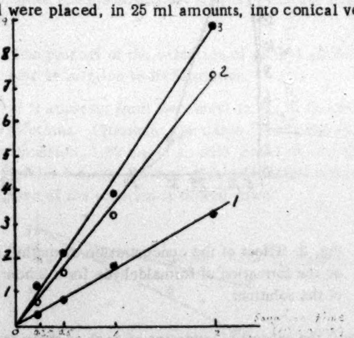

Fig. 1. Effect of sonation on the formation of formaldehyde in methyl alcohol solutions. 1) In 0.1% solution; 2) 0.5% solution; 3) in 1% solution.

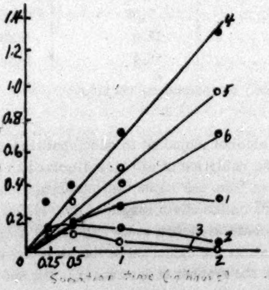

Fig. 2. Effect of sonation on the formation NO_2^- and NO_3^- in solutions of methyl alcohol. 1) NO_2^- in 0.1% solution; 2) NO_2^- in 0.5% solution 3) NO_2^- in 1% solution; 4) NO_3^- in 0.1% solution; 5) NO_3^- in 0.5% solution; 6) NO_3^- in 1% solution.

Nitrous and nitric acids [13], and formaldehyde [14] were determined colorimetrically in the alcohol solutions immediately after the action of the ultrasound. Ammonia was determined by a diffusion method [15]. The experiments were repeated not less than 3 times. Pure preparations of alcohols and triply distilled water were used for the preparation of the solutions. After a 2 hour sonation, 0.104 mg of NO_2^-, 1.58 mg of NO_3^-, and 1.99 mg of H_2O_2 formed in 100 ml of such water.

During the calculation of the acids formed, the amount of alkali necessary for the titration of the water subjected to the action of ultrasound under these conditions, was subtracted from the total alkali consumed for the titration of the sonated solutions.

The results of experiments on the action of ultrasonic vibrations on 0.1-1% solutions of methyl alcohol are given in Figs. 1 and 2. The curves show that an increase of formaldehyde formation occurs with increase of the sonation time. In addition, nitrous and nitric acids, products of the oxidation of nitrogen of the air dissolved in the water, are formed; the concentration of the nitrous acid first increases; then, as a result of its further oxidation, it decreases. The concentration of nitric acid continuously increases with the time of sonation.

The amount of nitrous and nitric acids, as well as formaldehyde, varies not only with the sonation time (Figs. 1 and 2), but also with the concentration of the alcohol.

With the same sonation time, the higher the concentration of the alcohol (within the limits of 0.1 to 1%), the greater the amount of formaldehyde formed, and the less that of nitrous and nitric acids. A peculiar relationship of the formation of formaldehyde to the concentration of the alcohol occurs with greater concentrations of methyl alcohol. Fig. 3 shows that the amount of formaldehyde formed increases with the concentration of the alcohol in solution, and reaches its greatest value in a 10% alcohol solution. Upon further increase of the concentration of the alcohol, its oxidation slows down, and the formation of formaldehyde decreases. In 50% alcoholic solution, the amount of formaldehyde is only 0.2 mg/ 100 ml. A similar relationship of the aldehyde formed to the concentration of the alcohol subjected to the action of ultrasound was found for ethyl alcohol [16].

The results of the effect of ultrasound on solutions of methyl, ethyl, n-propyl, and n-butyl alcohol are given in the table. The concentration of the alcohols was 0.02 molar, the sonation time, 3 hours.

It is apparent from the Table that aldehydes, whose quantities are calculated on the aldehyde groups, formed after a 3 hour sonation of solutions of the alcohols, increase from methyl to butyl alcohol. At the same time, the formation of nitric acid increases from ethyl to butyl alcohol. Data given above show that the longer the hydrocarbon chain of the alcohol, the more actively is the latter oxidized in the ultrasonic pole.

Alcohol	Aldehyde group *	NO_2^-	NO_3^-
	(in mg per 100 ml of solution)		
CH_3OH	5.80	Traces	0.96
C_2H_5OH	7.98	Traces	0.40
C_3H_7OH	16.5	None	0.20
C_4H_9OH	19.4	None	0.14

* Determined by iodometric titration.

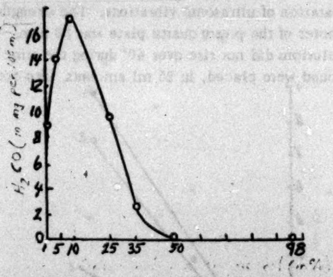

Fig. 3. Effect of the concentration of methyl alcohol on the formation of formaldehyde for a 2 hour sonation of the solutions.

The alcohol subjected to decomposition also has an effect on the oxidation of nitrogen dissolved in the liquid. It is apparent from the Table that the formation of nitric acid depends on the chain length of the alcohol. The longer the chain of carbon atoms, the more actively the alcohol prevents the oxidation of the dissolved nitrogen. The greater the amount of substances in the solution subjected to the oxidizing effect of ultrasound, the more strongly is the process of oxidation of each of these moderated.

The results obtained in this relation, which require further study, are illustrated by the sonation of alcoholic solutions of aminoacetic acid (glycine), as well as solutions of glucose and lactose.

The data on the effect of glycine on the oxidations of the alcohol are shown in Fig. 4.

It is apparent from the curves in Fig. 4 that the presence of glycine decreases the oxidation of methyl alcohol. Thus, with the increase of the concentration of glycine, the formation of formaldehyde decreases and approaches a limit at a concentration of glycine of 0.04 molar.

The processes of oxidation occurring as a result of the action of ultrasound also cause the decomposition of the amino acids [8]. Ammonia is formed, and, as a result of its subsequent oxidation, nitrous and nitric acids are formed; for this reason the amounts of the latter are greater in the alcoholic glycine solutions than in solutions of

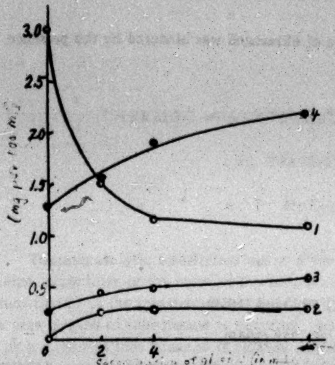

Fig. 4. Formation of H_2CO, NO_2^-, NO_3^-, and NH_3 in alcoholic solutions of glycine by the action of ultrasound. Concentration of methyl alcohol, 0.1%. Sonation time, 2 hours. 1) H_2CO; 2) NH_3; 3) NO_2^-; 4) NO_3^-.

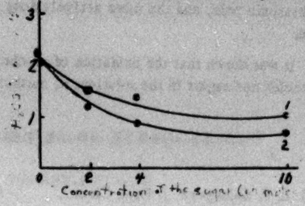

Fig. 5. Effect of ultrasound on the formation of H_2CO in methyl alcohol in the presence of sugars. Sonation time, 2 hours. 1) In the presence of glucose; 2) in the presence of latose.

the alcohol not containing the aminoacid.

Results of the action of ultrasound on the formation of formaldehyde in 0.1% solutions of methyl alcohol in the presence of glucose and lactose are given in Fig. 5. The curves show that the addition of sugars to solutions of methyl alcohol also causes a decrease in the formation of formaldehyde, which is greater with lactose than with glucose. The sonation of an 0.1% solution of methyl alcohol in which there was a mixture of glycine, glucose, and lactose each in concentrations of 0.02 molar, showed that the amount of formaldehyde formed under these conditions was 0.75 mg per 100 ml, i.e., less than in the presence of each of these substances alone.

The sugars themselves were subjected to oxidation by the action of ultrasonic vibrations [6, 7]. In the above reported experiments, 5.32 mg of COOH groups formed after a 2 hour sonation of an 0.1 M solution of glucose, which was 0.3% of the initial glucose (Fig. 5). The pH, equal to 6.66 initially, fell to 3.48 after the action of the ultrasound.

The product of the oxidation of methyl alcohol, formaldehyde, was subjected to further changes in the ultrasonic pole in relation to its formation.

It is apparent from the curves in Fig. 6 that the amount of formaldehyde decreases with the time of sonation of its solutions. Ultrasonic vibrations causing the oxidation of formaldehyde led to the formation of acids. After a 3 hour sonation, 1.82 mg of an acid, based on HCOOH, was formed in 100 ml of a formaldehyde solution. If a $4 \cdot 10^{-2}$ molar concentration of glycine is added to the solution of the aldehyde, the oxidation of formaldehyde by the action of the sonation is slowed down.

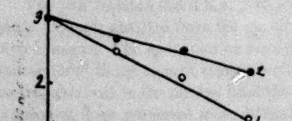

Fig. 6. Effect of sonation on solutions of formaldehyde. Initial concentration of formaldehyde, 3 mg per 100 ml. 1) Solution of H_2CO; 2) solution of H_2CO in the presence of $4 \cdot 10^{-2}$ M glycine.

The experimental material given in the present communication shows the complexity and the various forms of the chemical reactions occurring under the influence of ultrasound. This fact must be considered during examination of the problems of chemical and dispersive actions of ultrasonic vibrations.

SUMMARY

1. The action of ultrasound on aqueous solutions of methyl, ethyl, n-propyl, and n-butyl alcohols was studied.

2. It was shown that formaldehyde, nitrous and nitric acids were formed upon the sonation of solutions of methyl alcohol.

3. The longer the carbon atom chain in the alcohol molecule, the more readily was the latter oxidized in the ultrasonic pole, and the more actively does it "protect" the nitrogen of air dissolved in the liquid from oxidation.

4. It was shown that the oxidation of alcohols by the action of ultrasound was hindered by the presence of aminoacids and sugars in the solutions of methyl alcohol.

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THERMOCATALYTIC TRANSFORMATIONS OF HYDROCARBONS

III. TRANSFORMATION OF DIPHENYLMETHANE

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Thermocatalytic transformations of diphenylmethane hydrocarbons up to now have been insufficiently studied, especially in the cases of low temperature transformations. For benzene homologs this transformation results finally in the transposition of a radical from one molecule to the other, whereby the benzene ring with the least degree of substitution is liberated. With anhydrous aluminum chloride diphenylethane is transformed in such a manner that benzene is cleaved and the residue, benzil, adds to another molecule of diphenylethane with the formation of diphenethylbenzene. The analogous action of anhydrous aluminum chloride and aluminosilicates, on the one hand, and the possibility of comparing diphenylmethane with diphenylethane, on the other, led to the expectation that diphenylmethane with an aluminosilicate catalyst would undergo similar transformations related to the equilibrium between the products formed, i.e., benzene and dibenzylbenzene.

Experiments on the catalytic transformation of diphenylmethane were conducted in two ways: with the distillation of the volatile products formed, and in an autoclave, in both cases with activated gumbrin as the catalyst. In the experiments conducted at the usual pressures in an iron still, and in experiments in an autoclave, qualitatively identical results were obtained: benzene was obtained in the distillate, and substitution products of diphenylmethane in the residue, mainly p-dibenzylbenzene; therefore the reaction indeed proceeds as in the case of aliphatic benzene homologs, according to the scheme:

$$2C_6H_6CH_2C_6H_5 \longrightarrow C_6H_6 + C_6H_5CH_2C_6H_4CH_2C_6H_5.$$

EXPERIMENTAL

Experiments in an autoclave. Diphenylmethane and the catalyst, gumbrin activated by hydrochloric acid, were taken in a quantitative ratio of 1:1. Only three experiments were conducted, differing in the length of heating (1 hour and 45 min., 5 hours, 10 hours). The temperature was 200° in all experiments. At the end of the reaction, the products obtained were distilled, with the more volatile being distilled first at temperatures lower than used during the experiment; the catalyst was then extracted with benzene, after the removal of which, the residue was added to the previously distilled part.

The first fraction had a b.p. 79.5-81°, d_4^{20} 0.878. The yield of this fraction was about 95% of the more volatile products distilled from the autoclave, so that this part of the reaction products contained nothing in addition to benzene. The next fraction distilling at 81-300° contained almost exclusively unreacted diphenylmethane. It was isolated in the form of crystals with m.p. about 20° (pure diphenylmethane melts at 26°). A thick tarry mass was obtained in the residue from the distillation from which many crystals separated upon standing. The separation of these presented some difficulties, and for this reason, the residue above 300°, was vacuum distilled at 12 mm, and a fraction boiling at 245-250° (calculation for normal pressure gave about 405°) was obtained. The fraction distilled in this manner, rapidly crystallized and had an m.p. 86°. The following was found upon elementary analysis: C 93.15%; H 6.85%; M 256 261, 254. Calculated for $C_{20}H_{18}$: C 93.02%; H 6.98%; M 258. These results correspond to dibenzylbenzene which has m.p. 86°. Therefore, it was proven that the transformation of diphenylmethane proceeds according to the same scheme as for benzene homologs. The above method for the separation of the reaction mixture was also applied for the investigation of the products of the transformation of diphenylmethane at usual pressure.

Experiments at ordinary pressure. A series of experiments was conducted for the purpose of investigating the equilibrium between the starting and newly formed products of the reaction. The extent of the transformation was checked by the yields of benzene, since no other readily volatile products were obtained during the reaction.

The experiments were conducted in an iron still by heating to reflux at 120, 135, 150, and 170° in the liquid for long periods. After definite periods of time, the still was cooled, and a definite amount of the liquid products was removed with a pipette, and was investigated for benzene content by distillation to 90°. The distillate obtained was considered to be benzene, and its quantity calculated on the total amount of diphenylmethane used. Then the benzene along with the residue of its distillation, was returned to the still, and the heating was continued. In all, 24 experiments were conducted (see Table).

Yield of Benzene (in %) During the Transformation of Diphenylmethane at Various Temperatures and Heating Times

Experiment No.	Temperature	Heating time (in hours)	Yield of benzene (in %)	Experiment No.	Temperature	Heating time (in hours)	Yield of benzene (in %)
1	120°	2.5	0.49	13	150	5	9.03
2	120	5	1.40	14	150	10	9.20
3	120	10	2.32	15	150	15	9.30
4	120	15	2.39	16	170	0.5	6.80
5	135	1.25	3.62	17	170	1.25	9.0
6	135	2.5	5.60	18	170	2.5	10.5
7	135	5	6.10	19	170	5	11.3
8	135	10	6.30	20	170	10	11.6
9	135	15	6.40	21	170	15	11.5
10	150	0.5	2.90	22	200	1.75	20.0
11	150	1.25	6.50	23	200	5	21.7
12	150	2.5	8.06	24	200	10	21.8

The last three experiments in the above Table were conducted in an autoclave. Examination of the data in the Table shows that equilibrium is attained at the following yields of benzene: at 120°, after 10 hours with a yield of benzene of 2.3%; at 135°, after 5 hours with a yield of benzene of 11%, and at 200°, after approximately 2 hours with a yield of benzene of 21%. Actually, equilibrium was attained even at an earlier time, but the Table cannot be used to judge this time because the experiments were conducted with the removal of samples with rather longintermediate times. Calculated graphically: at 120°, about 10 hours, at 135°, about 4 hours, at 150°, about 3.5 hours, at 170°, about 3 hours, and at 200°, about 2.5 hours.

An attempt was also made to obtain diphenylmethane from benzene and dibenzylbenzene, i.e., to accomplish an equilibrium leading from the reaction products to the starting substances. Benzene and dibenzylbenzene in a ratio of 1:1 with an equal amount of activated clay was heated to reflux for 33 hours. The temperature of the mixture was initially equal to the boiling point of the mixture, i.e., 110°; after 33 hours, it increased to 116°, after which analysis of the mixture showed the presence of 7% of diphenylmethane in it. This experiment, however, cannot have any quantitative character, and an experiment in the autoclave, where it would have been possible to raise the temperature, would have been more conclusive.

The possibility of re-use of the activated gumbrin was checked in a series of experiments. A catalyst treated for a prolonged time at 135°, was used for the experiment. After washing it with benzene and drying at 250°, 100 g of such a catalyst and 100 g of diphenylmethane were heated for 2.5 hours at 170°; 10.4 g of benzene was obtained; this meant that the re-use of the catalyst was possible, and that the stopping of the reaction was caused by attainment of equilibrium, and not by poisoning of the catalyst.

SUMMARY

1. Diphenylmethane is very readily transformed into benzene and dibenzylbenzene in the presence of aluminosilicate catalyst even at 120°.

2. Methylbenzene was not formed at all during these transformations.

3. The transformation reaction has an equilibrium character, and diphenylmethane was formed by heating dibenzylbenzene with benzene.

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INVESTIGATIONS OF CONJUGATED SYSTEMS

I. SYNTHESIS AND PROPERTIES OF BROMOPRENE HOMOLOGS

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Recently, because of the discovery of outstanding rubbergenic properties of dienic halogen derivatives, many investigations have been conducted on the synthesis of these substances by various methods [1]. The synthesis and properties of halogen derivatives of butadiene have been studied in the greatest detail. There is a considerable blank, however, in regard to the homologs of the latter. This is especially true for the bromine compounds.

We decided to prepare a series of normal homologs of bromoprene, because of a previous study of the peculiarities of reactions of dienic halogen derivatives with alkyl hypohalites [2, 3]. The corresponding chloroprene homologs had previously been reported in the literature [4]. They were obtained by the reaction of homologs of vinylacetylene with hydrogen chloride in the presence of Cu_2Cl_2. Four homologs of bromoprene were obtained by an analogous method, the action of hydrogen bromide on alkylvinylacetylene in the presence of Cu_2Br_2.

These substances are colorless liquids with ethereal odors. Their constants are given in Table 1.

TABLE 1

Substance	Boiling point (in °)	Pressure (in mm)	d_4^{20}	n_D^{20}	MR_D	
					Found	Calculated
$CH_2{=}CH-CBr{=}CH_2$[5]	42-43	165	1.3970	1.4988	27.94	27.50
$CH_2{=}CH-CBr{=}CH_2-CH_3$ . .	67.5-68.5	120	1.3308	1.5113	33.11	32.12
$CH_2{=}CH-CBr{=}CH-C_2H_5$ . .	86.5-87	120	1.2706	1.5070	37.84	36.74
$CH_2{=}CH-CBr{=}CH-C_3H_7$ . .	64-65	20	1.2210	1.5040	42.46	41.36
$CH_2{=}CH-CBr{=}CH-C_4H_9$ . .	83-83.5	20	1.1829	1.5008	47.11	45.97

It is apparent from the data in Table 1 that there is a regular increase in the boiling point, decrease in the density, and in refractive index. All of the substances possess an exaltation in the molecular refractivity. Bromoprene deviates somewhat from its series of homologs: it has a considerably smaller refractive index and shows a smaller exaltation in the molecular refractivity. This is explained by the so-called "central disruption" of conjugation. This central disruption is leveled by the effect of the strongly polarizing system of substituents in the bromine homologs. A similar relationship occurs in the series of chloroprene and its homologs [1, 3]. The structure of the bromoprene homologs obtained was established on the basis of the study of their properties.

1) All of the substances polymerize and tar upon storage.

2) They eliminate bromine very slowly upon heating with alcoholic KOH solution.

3) They participate readily in dienic synthesis upon heating with esters of fumaric and maleic acids, and give the corresponding esters of alkylbromocyclohexenedicarboxylic acids, wherein the latter substances, like the starting ones, possess stability to alkalies in relation to the bromine atom.

4) A very intense frequency for the double bond of 1628 cm^{-1} was found in the Raman spectrum of ethylbromoprene. The frequency for the triple bond was absent.

The first two, and the fouth property of the substances obtained indicate the presence of a conjugated system of double bonds in their molecules. The third property indicates that the bromine atom is found at the double bond.

Therefore, the only acceptable formula of the six possible for the products of the addition of hydrogen bromide to homologs of vinylacetylene is $CH_2{=}CH-CBr{=}CH-R$.

EXPERIMENTAL

For the preparation of the bromoprene homologs, the authors initially applied a method used for the preparation of bromoprene from vinylacetylene. A mixture of the enynic hydrocarbon and a solution of Cu_2Br_2 in concentrated hydrobromic acid was shaken 8-10 hours. The yield of the alkylbromoprene was 10-15% under these conditions.

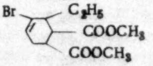
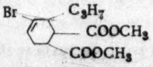
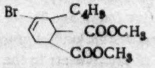
Better results were obtained by the addition of ammonium bromide or an amine hydrobromide to the reaction mixture. However, the yield of the alkylbromoprenes could not be raised above 30-35%. Thus, for example, 110 g of hexen-1-yne-2 was shaken for 10 hours with a solution of 110 g of Cu_2Br_2 in 375 g of a solution of hydrogen bromide saturated at 0° (d 1.64) into which 9 g of methylamine was passed initially. The reaction products were separated from the aqueous layer, washed with water, dried with $CaCl_2$, and vacuum distilled. Results of distillation at 120 mm: 1) to 78°, 62.5 g (starting hydrocarbon), 2) 78-85°, 1.3 g, 3) 86-88°, 44.2 g, 4) 89-90°, 3.8 g, 5) residue, 13 g.

Table 2 gives the analytical results for the bromoprene homologs.

TABLE 2

Substance	Sample (in g)	Weight of AgBr (in g)	% Br	
			Found	Calculated
$CH_2{=}CH-CBr{=}CH-CH_3$	0.1168	0.1494	54.43	54.36
$CH_2{=}CH-CBr{=}CH-C_2H_5$	0.1282	0.1508	50.05	49.62
$CH_2{=}CH-CBr{=}CH-C_3H_7$	0.1194	0.1293	46.08	45.65
$CH_2{=}CH-CBr{=}CH-C_4H_9$	0.1160	0.1164	42.70	42.24

TABLE 3

Substance		Boiling point at 10 mm (in °)	d_4^{20}	n_D^{20}	MR_D	
					Found	Calculated
	from the maleate	165 – 166	1.3796	1.5035	65.89	66.02
	from the fumarate	165 – 166	1.3693	1.5040	66.00	66.02
	from the maleate	169 – 170	1.3308	1.5000	70.57	70.64
	from the maleate	178.5 – 179.5	1.2996	1.4980	75.15	75.26
	from the fumarate	178 – 180	1.2926	1.4980	75.56	75.26

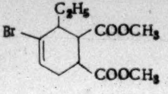
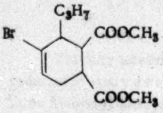
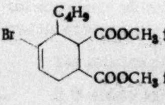
The condensation of the alkylbromoprenes with dimethyl fumarate and maleate was conducted in sealed tubes at 150° in toluene solution for 8 hours. These conditions were analogous to those generally used in the authors' laboratories during the study of the condensation of esters of unsaturated acids with dienic hydrocarbons.

A small amount of dimethyl fumarate was always obtained in addition to the condensation products, in reactions with the maleic ester. Evidently, under the conditions of the reaction, an isomerization of maleate to fumarate occurs, possibly, as a result of the catalytic effect of traces of hydrogen bromide separating from the alkyl bromoprene upon heating. For this reason, it is believed that the condensation products obtained from alkylbromoprenes and diethyl maleate were not pure cis isomers.

The dimethyl esters of the alkylbromocyclohexendicarboxylic acids, obtained as a result of this condensation, were viscous, colorless, almost odorless liquids. Table 3 gives the constants of several of the substances isolated.

Analytical results for these substances are given in Table 4.

TABLE 4

Substance	Sample (in g)	Weight of AgBr (in g)	Weight of AgI (in g)	% Br		% CH_3O	
				found	calculated	found	calculated
 from the maleate.	0.1163	0.0724	–	26.49	26.19	–	–
from the fumorate	0.1319	0.8826	–	26.65	26.19	–	–
	0.0835	–	0.1274	–	–	20.17	20.33
 from the maleate	0.1300	0.0777	–	25.43	25.04	–	–
	0.0866	–	0.1300	–	–	19.84	19.44
 from the maleate	0.1160	0.0679	–	24.91	23.98	–	–
	0.1584	–	0.2256	–	–	18.82	18.62
from the fumarate	0.1032	0.0584					
	0.0800	–	0.1120	–	–	18.50	18.62

1 g of ethylbromoprene was heated on the boiling water bath with a 10% KOH solution (double excess) in methanol for 1 hour. 0.0384 g or 7.7% of the bromine present in the sample went into solution. In an analogous experiment with butylbromoprene, 7.6% of bromine went into solution. The products of the condensation of bromoprene homologs with dimethylfumarate practically do not eliminate bromine under these conditions.

SUMMARY

1. A series of homologs of bromoprene was obtained by the action of hydrogen bromide in the presence of Cu_2Br_2 upon vinyl acetylene homologs.

2. The condensation of these substances with dimethyl maleate and fumarate was investigated.

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*See Consultants Bureau Translation, page 1557.

** See Consultants Bureau Translation, page 1091.

TERTIARY ACETYLENIC TRIOLS AND THEIR TRANSFORMATIONS

IV. DEHYDRATION OF 2,3,6-TRIMETHYLHEPTYNE-4-TRIOL-2,3,6.

V. I. Nikitin and A. Kh. Khamatov

Tertiary acetylenic glycerines, prepared by a method developed by one of the authors [1, 2], require a systematic study as a new, very interesting class of compounds. The molecule of such a glycerine, carrying three hydroxyl groups and an acetylenic bond, must possess the chemical properties of alcohols and glycols of the acetylenic series. On the other hand, certain peculiarities in the structure of these molecules must favor certain eccentricities in their chemical behavior, which are of theoretical and synthetic interest.

The relation of glycerines to dehydrating agents deserves attention.

It is widely known that γ-glycols, as well as acetylenic carbinols, lost water upon dehydration, with the formation of vinylacetylenic, or divinylacetylenic hydrocarbons.

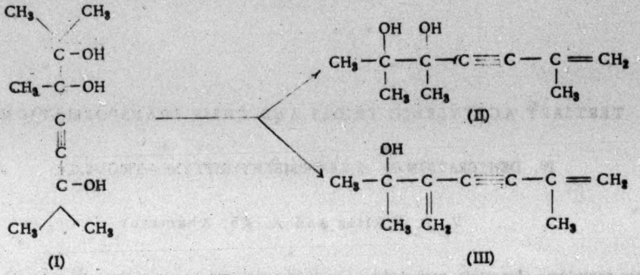
Du Pont, who first used dilute sulfuric acid for the dehydration of the acetylenic γ-glycol, tetramethylynediol [3], in addition to the main reaction product, diisopropenylacetylene, isolated dimethylisopropenylacetylenylcarbinol as an intermediate product resulting from the incomplete dehydration of the γ-glycol. Yu. S. Zalkind, E. D. Venus-Danilov and V. I. Ryabtseva [4] showed that the γ-glycol – asymmetrical dimethyldiphenylbutynediol – underwent a rearrangement into products isomeric to it under the action of an alcoholic solution of sulfuric acid. Depending upon the concentration of the acid, either a substituted tetrahydrofuranone or an α-diketone with an open chain of carbon atoms – 2-methyl-5,5-diphenylpentandiol-3, 4 was formed. Glycols underwent a pinacol rearrangement with more or less ease under these conditions, which was first discovered by A. M. Butlerov [5] for saturated pinacols and was studied later in detail by Meerwein [6].

A. E. Favorsky and A. S. Onishchenko [7] treated the acetylenic α-glycol, trimethylacetylenylethylene glycol, with concentrated sulfuric acid, and showed that the glycol mainly underwent a pinacoline rearrangement to form an acetylenic ketone which was hydrated at once into the saturated diketone, 3,3-dimethylpentadione-2, 4.

E. D. Venus-Danilova and coworkers [8, 9, 10] showed that certain acetylenic α-glycols underwent an acetylenyl-allenyl rearrengement under the action of sulfuric acid, as a result of which the unsaturated γ-keto alcohol was formed, which then cyclized into the substituted hydroxydihydrofurane. E. D. Venus-Danilova and L. A. Pavlova [11] also found that a pinacoline rearrangement occurred with the acetylenic α-glycol, methyldiphenyltertiarybutylacetylenylethyleneglycol. By treating it with 30% sulfuric acid, they isolated an acetylenic ketone, 3,3-diphenyl-6, 6-dimethylheptyne-4-one-2, which formed in addition to the products of the acetylenyl-allenyl rearrangement. I. N. Nazarov and I. V. Torgov [12] obtained two products by the distillation of a vinylacetylenyl α-glycol, trimethylvinylacetylenylethylene glycol, over potassium bisulfate: a dienynic carbinol, the product of the incomplete dehydration of the vinylacetylenyl α-glycol, and a vinylacetylenyl ketone, a result of the pinacoline rearrangement.

The results of the study of the action of dehydrating agents upon 2,3,6-trimethylheptyne-4-triol-2,3,6 (I) which is the simplest member of the tertiary acetylenic triols, is reported in the present communication.

Trimethylheptynetriol (I) was subjected to the dehydrating action of 20% sulfuric acid, potassium bisulfate, and p-toluene-sulfonic acid. The main product of the reaction, in all cases (from 40 to 62%) is the vinylacetylenyl α-glycol, trimethylisopropenylacetylenylethylene glycol (2,3,6-trimethylheptyne-4-ene-6-diol-2,3) (II) which was a glycerine-like liquid (b.p. 74-75° at 1.5 mm) obtained as a result of the loss of water from one of the hydroxyl groups of the acetylenyl triol. The dienynic carbinol, 2,6-dimethyl-3-methyleneheptyne-4-ene-6-ol-2 (III) was always present in small amounts (about 4-6% of the triol reacted) in the dehydration products. (A mobile liquid, boiling at 73-74° at 6 mm), it is the product of the dehydration of the heptynetriol with the participation of two of its hydroxyl groups:


(I) (II) (III)

The largest yield of the glycol (40% of the initial triol) was obtained with 20% acid upon dehydration with sulfuric acid. If 5-10% sulfuric acid was used for the reaction, a considerable part of the starting heptynetriol was recovered; a 30-50% acid caused a strong tarring.

The yield of the glycol (II) was 60-62% in the case of the dehydration of trimethylheptynetriol by vacuum distillation over potassium bisulfate, or p-tolunesulfonic acid.

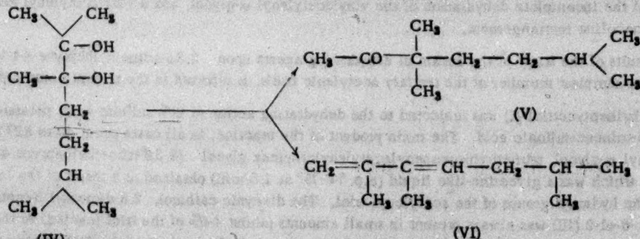
Therefore, tertiary acetylenic glycerines do not undergo the isomeric transformations, or pinacoline rearrangements under the conditions of the dehydration reaction, which could have been expected by analogy with α-glycols.

The structure of glycol (II) was proved by oxidation with a potassium permanganate solution; acetone, dimethylacetylcarbinol, formic acid, acetic acid, and oxalic acid were obtained. The structure of the dienynic alcohol (III), obtained with the glycol (II), was also proved by oxidation with potassium permanganate. Acetone, formic acid, acetic acid, and oxalic acid were obtained.

4 molecules of hydrogen were absorbed during the hydrogenation of the dienyne carbinol (III), which also confirmed its structure. The hydrogenation of trimethylisopropenylacetylenylethylene glycol (II), in the presence of a platinum catalyst in dry methanol solution, proceeded energetically at first, and then after the addition of 2 molecules of hydrogen, almost stopped. The product obtained distilled at 69-70° at 1.5 mm, and in all appearances, was an ethylenic α-glycol. It was hydrogenated further with the absorption of 1 molecule more of hydrogen into the completely saturated glycol (IV).

The saturated α-glycol, 2,3,6-trimethylheptanediol-2,3 (IV) (a crystalline product with m.p. 42-43°) obtained in this manner, underwent a pinacoline rearrangement by the action of sulfuric acid to give a ketone, 3,3,6-trimethylheptanone-2 (V) (a liquid with a pleasant odor with b.p. 65-67° at 11 mm), which readily formed a semicarbazone and 2,4-dinitrophenylhydrazone. The structure of ketone (V) as 3,3,6-trimethylheptanone-2 follows from the fact that a considerable amount of bromoform was obtained by oxidizing it with alkaline hypobromite.

In addition to the pinacoline rearrangement, the dehydration of glycol (IV) to the dienyic hydrocarbon, 2,3,6-trimethylheptadiene-1,3 also occurred partially; the latter could not be isolated in pure form. A fraction with b.p. 55-57° at 11 mm was obtained which contained ketone (V) as an impurity. It formed crystals with m.p. 134-135° with maleic anhydride; it could not be investigated further because of the small amount.


(IV) (V) (VI)

EXPERIMENTAL

The initial 2,3,6-trimethylheptyne-4-triol-2,3,6 was prepared, as reported by one of the authors [1], by the condensation of dimethylacetylenylcarbinol with dimethylacetylcarbinol and had an m.p. 82-83°.

I. Dehydration of 2,3,6-Trimethylheptyne-4-triol-2,3,6.

20% sulfuric acid. A mixture of 50 g of 2,3,6-trimethylheptyne-4-triol-2,3,6 and 200 ml of 20% sulfuric acid was heated for 2 hours on a boiling water bath in a flask with a reflux condenser. The reaction product was extracted with ether, treated with a dilute sodium carbonate solution, dried with sodium sulfate, and then after the removal of the ether, vacuum distilled at 2 mm:

Fraction 1 with b.p. up to 76°, 2.4 g, n_D^{20} 1.4960; fraction 2 with b.p. 76-77°, 18.0 g, n_D^{20} 1.4888. Tarry residue, 20.6 g.

The fraction with b.p. 76-77° at 2 mm was, as it was shown, trimethylisopropenylacetylenylethylene glycol (II); yield 40% of theory based on the trimethylheptynetriol used for the reaction.

Potassium bisulfate. A mixture of 20 g of 2,3,6-trimethylheptyne-4-triol-2,3,6, 7 g of potassium bisulfate, and 0.1 g of pyrogallol was heated at 3-4 mm to 150-155° on a metal bath. 15.9 g of a substance distilled at 70-110°; A total of 140 g of trimethylheptynetriol was dehydrated in several experiments, and 98.3 g of crude product was obtained.

The crude reaction product was dissolved in ether, and dried with sodium sulfate. After several vacuum distillations, the following fractions were isolated:

Fraction 1 with b.p. 74-75° at 7 mm, 4.8 g, n_D^{20} 1.5043 fraction 2 with b.p. 74-75° at 1.5 mm, 72.5 g, n_D^{20} 1.4888; fraction 3 with b.p. 115-120° at 1.5 mm, 10.5 g (crystals).

The fraction with b.p. 115-120° at 1.5 mm was the starting 2,3,6-trimethylheptyne-4-triol-2,3,6. The yield of the fraction with b.p. 74-75° at 1.5 mm was 62% based on the heptynetriol consumed.

p-Toluenesulfonic acid. A mixture of 25 g of 2,3,6-trimethylheptyne-4-triol-2,3,6, 0.08 g of p-toluenesulfonic acid, and 0.1 g of pyrogallol was heated to 150-155° at 3-4 mm on a metal bath; 21.8 g of product was distilled at 70-105°. 25 g more of the trimethylheptynetriol was dehydrated under these conditions, and 21.9 g of product was distilled.

The products of both experiments were combined, dissolved in ether, dried with sodium sulfate, and distilled at 1.5 mm:

Fraction 1 with b.p. to 72°, 7.3 g, n_D^{20} 1.4941; fraction 2 with b.p. 72-74°, 27.3 g, n_D^{20} 1.4887; fraction 3 with b.p. 74° and above, 3.7 g; residue, 5.3 g.

Fraction 3 was the unreacted starting trimethylheptynetriol. The yield of the main fraction with b.p. 72-74° at 1.5 mm was 60%.

The similar fractions of all experiments were combined and redistilled in vacuum. After several redistillations, two fractions were obtained:

Fraction 1 with b.p. 73-74° at 6 mm, n_D^{20} 1.5043; fraction 2 with b.p. 74-75° at 1.5 mm, n_D^{20} 1.4888.

1. Investigation of the Fraction with b.p. 73-74° at 6 mm.

d_4^{20} 0.9007, n_D^{20} 1.5043. Found: MR_D 49.34. $C_{10}H_{14}O$. Calculated: MR_D 46.97

0.1326 g substance: 0.3830 g CO_2; 0.1146 g H_2O. 0.1440 g substance: 0.4178 g CO_2; 0.1231 g H_2O. Found %: C 78.77, 78.96; H 9.67 9.56. $C_{10}H_{14}O$. Calculated %: C 80; H 9.33. 0.0992 g substance: 17 ml CH_4 (27°, 688.8 mm). 0.0990 g substance: 16.8 ml CH_4 (26.2° 688.8 mm). Found %: OH 10.75; 10.63; $C_{10}H_{14}O$. Calculated %: OH 11.3.

Oxidation. 200 ml of a 2% and then 700 ml of a 4% alkaline potassium permanganate solution (32 g of $KMnO_4$ calculated for 7 active oxygen atoms for 1 molecule of the substance) were added dropwise with mechanical stirring over a 7-hour period to 6.5 g of the substance in 60 ml of water. After the addition of all of the $KMnO_4$ solution, the manganese dioxide was filtered, and a distillate with the neutral substances was removed from the filtrate. The first drops of the distillate gave a 2,4-dinitrophenylhydrazone with m.p. 125-126° (from alcohol) with 2,4-dinitrophenylhydrazine. A mixed melting point with acetone 2,4-dinitrophenylhydrazone gave no depression. Other neutral substances were not detected.

The solution, after the removal of the neutral substances, was acidified with hydrochloric acid, and the volatile acids distilled with steam. 730 ml of a distillate was obtained which required 608.2 ml of 0.1 N NaOH containing 2.4 g of NaOH for neutralization. The presence of formic acid was established in the distillate by the calomel test, and that of acetic, by the cacodyl test

The volatile acids were converted into silver salts. The mixture of silver salts of formic and acetic acids was boiled with water for the decomposition of silver formate; the precipitated silver was filtered through a hot funnel, and the silver acetate, which precipitated in the filtrate, was analyzed.

0.0962 g salt: 0.0619 g Ag. 0.0876 g salt: 0.0564 g Ag. Found %: Ag 64.40, 64.31. CH_3COOAg. Calculated %: AG 64.65.

The solution remaining after the removal of the volatile acids, was extracted for 3 days with ether in an extractor. 1 g of oxalic acid with m.p. 101-102° was isolated from the ether extract. A mixed melting point with authentic oxalic acid gave no depression.

Therefore, the following were obtained as a result of the oxidation: acetone, formic acid, acetic acid, and oxalic acid.

Hydrogenation. 0.66 g of the substance, dissolved in 20 ml of dry methanol, was hydrogenated over platinum oxide (according to Adams) for 3 hours. 370 ml of hydrogen was absorbed at 20° and 694 mm. Calculated for 4 moles of hydrogen, 384 ml.

According to the results of the oxidation and the hydrogenation, the fraction boiling at 73-74° at 6 mm, n_D^{20} 1.5043, was the dienynic carbinol, 2,6-dimethyl-3-methyleneheptyne-4-en-6-ol-2 (III).

The incomplete agreement of the results of the elementary analysis with calculated must be explained by the presence of some vinylacetylenic glycol (II) as an impurity.

2. Investigation of the Fraction with b.p. 74-75° at 1.5 mm.

n_D^{20} 1.4888, d_D^{20} 0.9696. Found: MR_D 49.99. $C_{10}H_{16}O_2$. Calculated: MR_D 48.96. 4.925 mg substance: 12.882 mg CO_2; 4.255 ml H_2O. 3.850 mg substance: 10.054 mg CO_2; 3.294 mg H_2O. Found %: C 71.38, 71.27; H 9.67, 9.57. $C_{10}H_{16}O_2$. Calculated %: C 71.43; H 9.52. 0.1120 g substance: 38.4 ml CH_4 (34°, 685.1 mm). 0.1126 g substance: 38.6 ml CH_4 (35°, 685.1 mm). Found %: OH 20.83, 20.89. $C_{10}H_{16}O_2$. Calculated %: OH 20.24.

Oxidation. 19.1 g of the substance in 100 ml of water was used and 2370 ml of a 3% potassium permanganate solution (71 g of $KMnO_4$ calculated for 6 active oxygen atoms per mole of the substance isolated) was added dropwise with efficient stirring over a period of 7 hours.

The neutral substances were distilled with steam. The distillate with the neutral substances was concentrated by means of gradual distillation to 250 ml; acetone with b.p. 53-56°, 0.8 g, was obtained from the distillate with a rectifying column. It gave a semicarbazone with m.p. 187-188° with semicarbazide hydrochloride. A mixed melting point with authentic acetone semicarbazone gave no depression. The solution remaining after the distillation of the acetone was extracted for 3 days with ether in an extractor. The ether extract was dried with sodium sulfate, and distilled after the removal of the ether. 1.2 g of a substance distilled (b.p. 132-135°, n_D^{20} 1.4120), which was dimethylacetylcarbinol which gave a semicarbazone melting at 160-161°. A mixed melting point with authentic dimethylacetylcarbinol semicarbazone did not give a depression.

The solution of salts, after the removal of the neutral substances, was acidified with sulfuric acid, and the volatile acids steam distilled. The volatile acids were extracted with ether from the distillate. After drying and the removal of the ether, three fractions were collected:

Fraction 1 with b.p. 90-96°, 1.3 g; fraction 2 with b.p. 96-110°, 0.6 g; fraction 3 with b.p. 110-115°, 3.1 g.

The fraction with b.p. 90-96° contained formic acid, which was qualitatively established by a calomel test.

The fraction with b.p. 110-115° was acetic acid, as was established by the formation of cacodyl oxide and the preparation of a silver salt.

0.0372 g salt: 0.0238 g Ag. 0.1180 g salt: 0.0758 g Ag. Found %: Ag 64.00, 64.23. CH_3COOAg. Calculated %: Ag 64.65.

3.5 g of oxalic acid with m.p. 101-102° was isolated from the non-volatile acids (mixed melting point).

Therefore, as a result of the oxidation of the fraction with b.p. 74-75° at 1.5 mm, the following were obtained: acetone, dimethylacetylcarbinol, and formic, acetic, and oxalic acids.

The results of the oxidation as well as other results of the investigation of the fraction with b.p. 74-75° at 1.5 mm, showed that the latter was a substituted vinylacetylenic α-glycol trimethylisopropenylacetylenylethylene glycol (II).

Hydrogenation of trimethylisopropenylacetylenylethylene glycol. 6.65 g of the substance dissolved in 60 ml of dry methanol was hydrogenated over platinum oxide (according to Adams) at 12° and 698 mm. After the addition of 2 moles of hydrogen, a sharp decrease in the absorption of hydrogen occurred. 2250 ml of hydrogen was absorbed within 2 hours 20 min. (calculated for 2 moles, 2010 ml).

The experiment was repeated with 8.6 g of the substance in 60 ml of dry methanol.

After the removal of the methanol, the hydrogenation products of two experiments were combined and distilled at 69-70° at 1.5 mm. 14.5 g of a substance, n_D^{20} 1.4610, was obtained, which was then hydrogenated in a solution of 50 ml of glacial acetic acid over platinum oxide. 1980 ml of hydrogen was absorbed at 15° and 698.3 mm (calculated 2180 ml). Therefore, a total of 3 moles of hydrogen were consumed by 1 mole of the substance.

The completely hydrogenated product was extracted with ether after the neutralization of the acetic acid, dried over potassium carbonate, and distilled at 1.5 mm:

Fraction 1 with b.p. to 72°, 0.8 g, n_D^{20} 1.4570; fraction 2 with b.p. 72-76°, 12.5 g, n_D^{20} 1.4598; residue, 0.8 g.

Upon redistillation of fraction 2, 11.5 g of a substance with b.p. 67-68° at 1 mm was obtained.

n_D^{20} 1.4522; d_4^{20} 0.9101. Found: MR_D 52.77. $C_{10}H_{22}O_2$. Calculated: MR_D 52.63.

This fraction crystallized upon standing, and melted at 42-43° after recrystallization from benzene.

11.10 mg substance: 28.06 mg CO_2; 12.25 mg H_2O. 9.07 mg substance: 22.95 mg CO_2; 10.19 mg H_2O. Found %: C 68.99, 69.05; H 12.35, 12.56. $C_{10}H_{22}O_2$. Calculated %: C 68.90; H 12.73. 0.1294 g substance: 39.3 ml CH_4 (20°, 589.9 mm). 0.1140 g substance: 34.2 ml CH_4 (21.5°, 689.9 mm). Found %: OH 19.54, 19.21. $C_{10}H_{22}O_2$. Calculated %: OH 19.54.

Therefore, the fraction with b.p. 67-68° at 1 mm, n_D^{20} 1.4522, was 2,3,6-trimethylheptandiol-2,3 (V).

II. Dehydration of 2,3,6-trimethylheptandiol-2,3 (V).

A mixture of 17 g of the substance in 300 ml of 25% sulfuric acid was heated on the water bath for 4 hours at 80-90°. The reaction products were extracted with ether, neutralized with sodium carbonate, dried with sodium sulfate, and distilled at 11 mm to yield the two fractions:

Fraction 1 with b.p. 55-57°, 3.5 g, n_D^{20} 1.4552; fraction 2 with b.p. 65-67°, 7.8 g, n_D^{20} 1.4260.

1. Investigation of the Fraction with b.p. 55-57° at 11 mm

d_4^{20} 0.7923, n_D^{20} 1.4552. Found: MR_D 47.28. $C_{10}H_{18}F_2$. Calculated: MR_D 47.43. 0.1602 g substance: 0.4664 g CO_2; 0.1794 g H_2O. 0.1531 g substance: 0.4550 g CO_2; 0.1725 g H_2O. Found %: C 79.45, 81.04; H 12.54, 12.60. $C_{10}H_{18}$. Calculated %: C 86.96; H 13.07.

Hydroxyl groups were not found by the method of Chugaev-Tserevitinov.

Condensation with maleic anhydride. 0.75 g of the substance with 0.7g maleic anhydride in 6 ml of toluene was heated for 20 hours at 110-120° in a sealed tube. After removal of the solvent, the crystals which formed were filtered and washed with hot chloroform to remove the unreacted maleic anhydride. 0.2 g of crystals were obtained which were recrystallized from dichloroethane with the addition of several drops of methanol. The crystals melted at 134-135°, and were not subjected to further investigation because of the small amount.

On the basis of these results it can be concluded that the fraction with b.p. 55-57° at 11 mm was dienic hydrocarbon of structure (V) contaminated with a higher boiling ketonic fraction.

This conclusion was also confirmed by the fact that a small amount of semicarbazone was formed by treating the fraction with b.p. 55-57° at 11 mm with semicarbazide. However, the hydrocarbon purified by means of the semicarbazone could not be isolated because it completely polymerized into a light yellow glass-like mass upon an attempt to vacuum distill it.

2. Investigation of the Fraction with b.p. 65-67° at 11 mm.

d_4^{20} 0.8303; n_D^{20} 1.4260. Found: MR_D 48.12. $C_{10}H_{20}O$. Calculated: MR_D 48.39.
0.1770 g substance: 0.4950 g CO_2; 0.2024 g H_2O. 0.1208 g substance: 0.3380 g CO_2: 0.1402 g H_2O.
Found %: C 76.26, 76.32; H 12.79, 12.98. $C_{10}H_{20}O$. Calculated %: C 76.84; H 12.85.

A semicarbazone with m.p. 132-133° (from 50% aqueous alcohol) was obtained in the form of needle-like crystals.

2.581 mg substance: 0.445 ml N_2 (26°, 750 mm). 4.484 mg substance: 0.772 ml N_2 (25°, 747 mm).
Found %: N 19.43, 19.43. $C_{11}H_{23}ON_3$. Calculated %: N 19.71.

A 2,4-dinitrophenylhydrazone with m.p. 112-113° (from alcohol) was obtained in the form of gold-like scales.

4.663 mg substance: 0.667 ml N_2 (21°, 743 mm). 4.383 mg substance: 0.640 ml N_2 (23°, 745 mm).
Found %: N 16.25, 16.51. $C_{16}H_{24}O_4N_4$. Calculated %: N 16.67.

Oxidation with alkaline hypobromite. 17.2 g of bromine was slowly added dropwise at −10° with mechanical stirring to a mixture of 5.6 g of the substance and 4.3 g of sodium hydroxide in 17 ml of water. After the addition of the bromine, the stirring was continued for 1.5 hours more. The mixture was then treated with thiosulfate and the neutral substances extracted with ether. The ether extracts were dried over potassium carbonate, and after the removal of the ether, 8.3 g of a substance was obtained which was distilled at ordinary pressure. A fraction, 5.5 g, was collected at 146-148°; this fraction was bromoform according to the boiling point and the character of its odor.

The obtaining of bromoform by the oxidation of fraction with b.p. 65-67° at 11 mm, as well as other results of the investigation, indicated that it was the ketone, 3,3,6-trimethylheptanone-2 (V).

SUMMARY

1. The dehydration reaction of 2,3,6-trimethylheptyne-4-triol-2,3,6 proceeded mainly with the elimination of only 1 molecule of water from the molecule of the alcohol to form a substituted vinyl-acetylenic α-glycol.

2. The hydroxyl groups linked with two neighboring carbon atoms in the molecule of the tertiary triol possessed a great stability to the action of dehydrating agents.

3. Four new substances unreported in the literature were obtained: 2,3,6-trimethylheptyne-4-ene-6-diol-2,3 (trimethylisopropenylacetylenylethylene glycol), 2,6-dimethyl-3-methyleneheptyne-4-en-6-ol-2, 3,6-trimethylheptandiol-2,3, and 3,3,6-trimethylheptanone-2.

4. 2,3,6-Trimethylheptandiol-2,3 underwent a pinacoline rearrangement under the action of dehydrating agents to form the corresponding ketone, 3,3,6-trimethylheptanone-2.

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* See Consultants Bureau Translation, p. 1197.

** See Consultants Bureau Translation, p. 2309.

*** See Consultants Bureau Translation, p. a-197.

**** See Consultants Bureau Translation, p. 87.

1,1-DIMETHYLCYCLOPROPANE

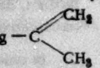
Ya. M. Slobodin, V. I. Grigoryeva, and Ya. E. Shmulyakovsky

Cyclopropane hydrocarbons, according to their properties, occupy an intermediate position between the saturated and unsaturated hydrocarbons. They are capable of adding halogens and hydrogen halides. They are comparatively easily subjected to hydrogenation.

The addition of the hydrogen halide acids proceeds with great speed and in accordance with Markovnikov's rule, and leads to the cleavage of the bond in the three membered ring adjacent to the carbon atom which contains substituents [1, 2, 3].

The addition reaction of halogens with the cyclopropane hydrocarbons proceeds more complexly and leads most often to the formation of a mixture of products. The action of bromine on 1,1-dimethylcyclopropane was first studied by Gustavson [2]. He assigned the structure of 2,4-dibromo-2-methylbutane to the bromide formed on the basis of the fact that trimethylethylene was formed by the removal of bromine from it. This corresponded to the literature data [4] on the removal of bromine from 2,4-dibromo-2-methylbutane. However, later [5], it was shown that the hydrocarbon formed by the removal of bromine from 2,4-dibromo-2-methylbutane has erroneously been accepted as being trimethylethylene. Actually it is isopropylethylene.

In the present investigation the bromides formed by the action of bromine on 1,1-dimethylcyclopropane, as well as the hydrocarbons obtained by the removal of bromine from these dibromides, were studied.

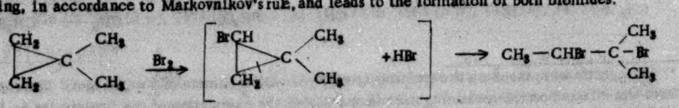
Two lines with frequencies of 1652 cm^{-1} and 1680 cm^{-1} were found in the Raman spectrum of the hydrocarbon formed by the action of zinc dust upon the bromides obtained from 1,1-dimethylcyclopropane. The ratio of the intensities of these frequencies was 3:2. The frequency 1680 cm^{-1} can be caused by the double bond of a trisubstituted ethylene. For a hydrocarbon of the composition C_5H_{10}, this can only be trimethylethylene. The frequency 1652 cm^{-1} indicated the presence of a component in the hydrocarbon which contains the grouping  $-C\begin{matrix}\diagup CH_2 \\ \diagdown CH_3\end{matrix}$ For a hydrocarbon of the composition C_5H_{10}, only asymm. methylethylethylene can have this grouping. On the basis of visual evaluation it can be concluded that the obtained mixture of hydrocarbons contains about 40% of trimethylethylene and about 60% of asymm. methylethylethylene.

It could be expected that the bromides formed by the action of bromine upon 1,1-dimethylcyclopropane contained 40% of trimethylethylene bromide and 60% of asymm. methylethylethylene bromide, respectively. Raman spectra were made for verification. Table 1 gives the spectral data: the bromides obtained from 1,1-dimethylcyclopropane, and from a mixture consisting of 40% trimethylethylene bromide and 60% asymm. methylethylethylene bromide.

The practically complete identity of the spectra given in Table 1 proves the composition of the products of the bromination of 1,1-dimethylcyclopropane qualitatively and quantitatively.

The results obtained show that the reaction between bromine and dimethylcyclopropane proceeds quite complexly. It can be thought that in the first phase of the reaction bromine substitutes a hydrogen in the cyclopropane ring, as well as in the methyl group of the side chain. The hydrogen bromide formed adds at once to the cyclopropane ring, in accordance to Markovnikov's rule, and leads to the formation of both bromides.

(I)



(II)

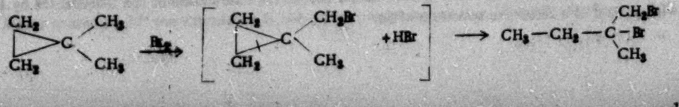


TABLE 1
Raman Spectra* of the Bromides
(frequencies in cm^{-1}

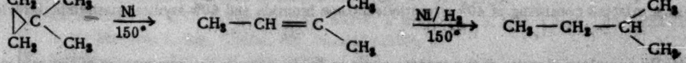
Bromides from 1,1-dimethylcyclopropane	40% trimethylethylene bromide, 60% asymm. methylethylethylene bromide	Bromides from 1,1-dimethylcyclopropane	40% trimethylethylene bromide, 60% asymm. methylethylethylene bromide	Bromides from 1,1-dimethylcyclopropane	40% trimethylethylene bromide, 60% asymm. methylethylene bromide
183(10)	184(8)	619(8)	618(8)	1026(2)	
294(5 w)	292(4 w)	634(10)	634(10)	1053(3)	1054(2)
322(2)	323(3)	655(1)	665(1)		1078(0.5)
387(2)	385(3 w)	682(1)		1100(4)	1105(5)
423(1)	418(0.5)	700(1)	703(1)	1167(3)	1167(4)
442(2)	437(0.5)	765(7)	765(8)	1208(2)	1210(2)
468(2)	466(2)	797(5)	797(7)	1224(5)	1227(6)
494(3)	493(3)	835(2)		1285(3)	1286(2)
517(2)	514(1)	863(4)	863(2 w)	1383(2)	1384(1 w)
543(2)	543(2)	880(2)			1431(4)
563(2)	560(2)	938(4)	936(2)	1445(4 w)	1453(3)

The problem of hydrogenation of cyclopropane hydrocarbons also is rather complex. Part of the known facts indicate that the hydrogen adds to the bond adjacent to the substituted carbon of the ring; another part of the known facts showsthat the addition of hydrogen also occurs at the bond opposite to the substituted carbon of the ring.

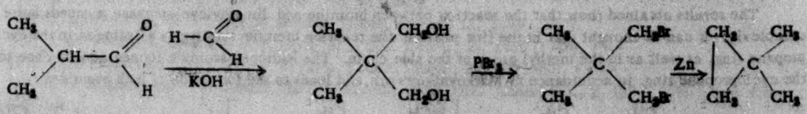
Thus Rozanov [3] obtained isopentane by hydrogenation of ethylcyclopropane. Isopropylcyclopropane, upon hydrogenation, was transformed into a mixture consisting mainly of 2,3-dimethylbutane [7], while isopropenylcyclopropane was converted into isohexane upon hydrogenation [8]. Kizhner [9] obtained a mixture of two hydrocarbons upon hydrogenation of 1-methyl-2-isoproplycyclopropane. 1,1,2-Trimethylcyclopropane formed a mixture of the three possible products upon hydrogenation [10].

The hydrogenation of 1,1-dimethylcyclopropane over a nickel catalyst, deposited on kieselguhr, at 150°, was studied in the present investigation. Isopentane without any noticeable contamination of the other hydrogenation product, neopentane, was obtained as a result. Therefore, the hydrogen added to the bond adjacent to the substituted carbon atom of the ring.

In order to determine the mechanism of hydrogenation, experiments with insufficient amounts of hydrogen were conducted. An intense line with a frequency of 1680 cm^{-1} appeared in the Raman spectra of the products obtained, which indicated the presence of considerable amounts of trimethylethylene in the mixture. In addition, all of the intense frequencies of 1,1-dimethylcyclopropane were retained in the spectra. This fact made is possible to suppose that the first act in these experiments on hydrogenation was the isomerization of 1,1-dimethylcyclopropane into trimethylethylene which was hydrogenated to isopentane:



The synthesis of the starting 1,1-dimethylcyclopropane was accomplished according to the scheme [13]:



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* The spectra were taken on the spectrograph ISP-51 with a camera of f = 270 mm. The measurement of the lines was effected on the measuring microscope IZA-2, the calculation of the frequencies by Hartman's formula with the aid of a reference spectrum of Fe.

TABLE 2
Raman Spectra of the Hydrocarbons
(frequencies in cm^{-1})

Isopentane [11]	Products of the hydrogenation of 1,1-dimethylcyclopropane	Neopentane	Isopentane	Products of the hydrogenation of 1,1-dimethylcyclopropane	Neopentane
367(3)	361(2)	335(10)	1295(2)	1295(2)	
464(6)	460(5)	414(3)	1337(3 w)	1337(3 w)	
764(10)	764(10)	733(20)	1353(3 w)	1353(3 w)	1455(15)
796(8)	795(8)		1446(9 w)	1446(8 w)	2712(5)
909(5)	908(4 w)	925(15 w)	2721(2)	2721(1)	2745(3)
954(3)	951(2)		2735(1)		2794(3)
986(0)	986(3)		2854(12)	2854(8)	2864(7)
1014(3 w)	1011(3)		2875(31)	2871(20)	2892(5)
1035(5)	1035(4)		2909(13 h)	2910(10)	2911(10)
1147(4)	1146(4)		2935(17 h)	2935(12)	2937(3)
1177(4 s)	1179(4)		2965(18)	2961(12)	2955(3)
1267(1)	1265(1)	1252(20 w)			

EXPERIMENTAL

2,2-Dimethylpropanediol-1,3

The diol was prepared by the condensation of isobutyraldehyde with formaldehyde in a solution of alcoholic alkali [13].

A solution of 35 g of KOH in 150 ml of alcohol was placed into a flask equipped with a stirrer and reflux condenser. A mixture of 30 ml of alcohol, 36 g of isobutyraldehyde, and 130 ml of 28% formaldehyde was added to the solution at 40° with efficient stirring over a 2 hour period. The flask was then heated for 18 hours at 80°; After the distillation of the alcohol, the residue in the flask was extracted for 5-6 hours with ether. The ether was removed. The diol was vacuum distilled.

B.p. 201-204° at 760 mm; m. p. 126°. Found %: C 57.73; H 11.68. $C_5H_{12}O_2$. Calculated %: C 57.69; H 11.63.

A total of 600 g of diol was prepared. The yield of the pure product was 50% of theory.

1,3-Dibromo-2,2-dimethylpropane.

0.25 mole of the diol was placed into a flask and 0.25 mole of PBr_3 was added dropwise to it with cooling with ice water [14]. The temperature of the bath was then slowly raised to 100°. The water bath was replaced by an oil bath, and the mixture was kept for 18 hours at 150°. The contents of the flask were poured into cold water after cooling. The bromide was extracted with ether. The ether solution was washed with water and dried. After the removal of the ether, the bromide was distilled.

B.p. 182-183° at 743 mm and 14 mm; d_4^{20} 1.6775; n_D^{20} 1.5047; MR_D 40.63. Found %: Br 68.60. $C_5H_{10}Br_2$. Calculated %: Br 69.60; MR_D 41.05.

The yield of the bromide was 40% of theory. A total of 420 g of the substance was prepared.

Raman Spectrum

167 (2), 212 (2), 274 (8), 330 (3), 372 (1), 404 (1), 443 (7), 594 (0.5), 644 (10), 668 (8), 703 (5), 756 (0.5), 863 (3), 904 (2), 916 (3), 959 (3 w), 1078 (2), 1122 (2), 1209 (0.5), 1265 (5 w), 1429 (4), 1459 (4).

1,1-Dimethylcyclopropane

1 Mole of zinc dust, 90 ml of alcohol, and 5 ml of water were placed into a flask with a reflux condenser and dropping funnel. The mixture was heated to boiling, and then 0.25 mole of 1,3-dibromo-2,2-dimethylpropane was slowly added. Water heated to 60° was circulated in the reflux condenser because of which the vapors of the

hydrocarbon formed passed through the condenser uncondensed, and entered a well-cooled coil. The hydrocarbon was washed with water, dried, and distilled over metallic sodium. Yield 90-95% of theory based on the dibromide.

B.p. 21°; d_4^{20} 0.6618 (in a closed pycnometer); n_D^{20} 1.3663; MR_D 23.69. C_5H_{10}. Calculated: MR_D 23.79. (The increment for the three membered ring was taken to be equal to 0.7)

Raman Spectrum

172 (1), 182 (1), 356 (3 w), 396 (2), 632 (1), 685 (8), 735 (0.5), 786 (1), 836 (6), 930 (10), 1058 (7), 1125 (2), 1183 (1), 1214 (2), 1230 (3), 1290 (1), 1321 (9), 1388 (0.5), 1432 (4), 1459 (4), 2737 (3), 2869 (8) 2895 (7), 2930 (6), 2956 (5), 2998 (20), 3061 (4 w).

The present spectrum is identical to that obtained by Cleveland [15].

Action of Bromine Upon 1,1-Dimethylcyclopropane

13 g of the hydrocarbon was placed into a flask with a reflux condenser, and 31.5 g of bromine was slowly added with cooling with ice water. The reaction proceeded violently. The bromide was separated, dried over calcium chloride, and distilled. A dibromide with b.p. 64.5° at 18 mm (82%) and a tribromide with b.p. 110-114° at 17 mm (18%) were isolated.

Properties of the dibromides: d_4^{20} 1.6440; n_D^{20} 1.5059; MR_D 41.60. Found %: Br 69.07. $C_5H_{10}Br_2$. Calculated: MR_D 41.05; % Br 69.60.

The Raman spectrum is given in Table 1.

Properties of the tribromide: d_4^{20} 1.8761; n_D^{20} 1.5366.

Removal of Bromine from the Dibromide

The bromine was removed in the usual manner by the action of zinc dust in alcoholic medium. Yield of the hydrocarbon: 73%.

B.p. 30.5-33°; d_4^{20} 0.6530; n_D^{20} 1.5366.

Raman Spectrum

265 (1), 348 (1), 396 (2), 439 (2), 526 (3 w), 593 (3 w), 611 (1), 769 (10), 924 (1), 1012 (1 w), 1189 (1), 1240 (1), 1332 (2), 1389 (3), 1428 (1), 1455 (3), 1594 (1), 1618 (2), 1652 (8), 1680 (6).

Hydrogenation of 1,1-Dimethylcyclopropane

The hydrogenation was effected in a flowing system. The catalyst was nickel deposited on kieselguhr. The experiment temperature was 150°. The catalyst was initially heated for 5 hours at 350° in a stream of hydrogen.

The hydrogen was passed through a graduated vessel containing the hydrocarbon. Due to the high volatility, the hydrocarbon vapor was entrained by the hydrogen, and the mixture entered into the reaction tube. The amount of hydrocarbon in the gaseous phase was regulated by cooling the vessel. The rate of passage of the hydrogen was measured with a flow meter. The rate of the introduction of the hydrocarbon was measured by means of its removal from the vessel. The volume velocity of the hydrogen was 150 liters per liter of catalyzate per hour. The products of the hydrogenation were collected in a trap cooled by dry ice. The hydrocarbon was dried and distilled. The Raman spectrum is given in Table 2.

B.p. 27.5-28°; d_4^{20} 0.6185; n_D^{20} 1.3537. (Literature data for isopentane [16]: d_4^{20} 0.6197; n_D^{20} 1.3539).

In separate experiments, hydrogenation was conducted with an insufficient amount of hydrogen. The reaction products boiled at 25-35°.

Raman Spectrum of the Hydrogenation Products

334 (1), 358 (3 w), 392 (2 w), 444 (1), 462 (1), 528 (3), 630 (1), 665 (1), 685 (8), 767 (8), 800 (2), 838 (7), 874 (1), 933 (10), 1061 (7), 1126 (0.5), 1232 (2), 1289 (1), 1322 (7), 1343 (2), 1386 (6), 1452 (7), 1680 (7), 2738 (0.5), 2865 (7), 2895 (1), 2923 (5), 2934 (5), 2965 (4), 2999 (8), 3064 (2).

* Only isopentane was obtained as a reaction product upon a repeat of the hydrogenation.

SUMMARY

1. By the action of bromine upon 1,1-dimethylcyclopropane, a mixture of bromides containing 40% trimethylethylene bromide and 60% asymm. methylethylethylene bromide was formed.

2. The removal of bromine from the mixture of bromides obtained led to the formation of trimethylethylene and asymm. methylethylethylene in the same ratio.

3. Hydrogenation of 1,1-dimethylcyclopropane over nickel on kieselguhr at 150° led to the formation of isopentane.

4. By hydrogenation of 1,1-dimethylcyclopropane with an insufficient amount of hydrogen, the hydrocarbon mixture, in addition to unchanged 1,1-dimethylcyclopropane, contained trimethylethylene.

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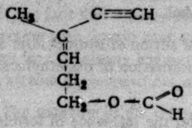
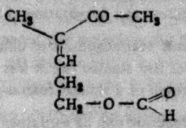
MECHANISM OF THE TRANSFORMATION OF TERTIARY CYCLOPROPANE ALCOHOLS UNDER THE EFFECT OF MINERAL AND ORGANIC ACIDS

I. REACTION OF DIMETHYLCYCLOPROPYLCARBINOL WITH FORMIC ACID

T. A. Favorskaya and N. V. Shcherbinskaya

The reaction of formic acid with methylacetylenylcyclopropylcarbinol [1], methylethylcyclopropylcarbinol, and methylphenylcyclopropylcarbinol [2] was studied in previous investigations. In the first case, the formate of the primary enyne alcohol (I) and the product of its hydration, the ester of the ketoalcohol were obtained (II)


(I)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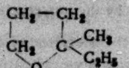
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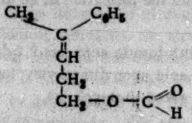
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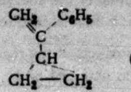
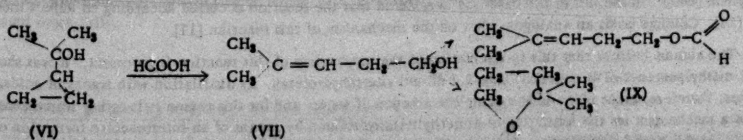

(V)

In the second case, the γ-oxide of methylethyltetramethylene, or 2,2-methylethyltetrahydrofurane (III) was obtained; in the third, the formate of the unsaturated alcohol (IV) and the product of the dehydration of the cyclic alcohol, asymm. phenylcyclopropylethylene (V). In all of these cases the concentration of formic acid was not lower than 80%, and the reaction was conducted with heating. Because of the sufficiently forcing reaction condition, no intermediate products were isolated in all three cases, and for this reason, all of the suggestions on the mechanism of the reactions were not final.

Milder conditions were used during the study of the reaction of dimethylcyclopropylcarbinol with formic acid: 50% instead of 80% formic acid was used; as a result a complex mixture of products was obtained from which five compounds were isolated whose structures were accurately determined, which made it possible to establish the general mechanism of the reaction of the alcohols studied with formic acid.

The first product of this reaction was the unsaturated primary alcohol, 2-methylpentene-2-ol-5 (VII), formed as a result of the intermolecular allylic rearrangement of the tertiary cyclic alcohol (VI) accompanied by the moving of the hydroxyl to the β-position, and the opening of the three membered ring


(VI) (VII) (VIII) (IX)

A similar type of allylic rearrangement was first discovered by A. E. Favorsky and L. A. Dyakonov [3], during a study of the action of phosphorous pentachloride upon acetyltrimethylene: the initially formed cyclic dichloride isomerizes into an ethylene derivative by means of the movement of one of the chlorine atoms into the β-position, and the opening of the ring.

The unsaturated alcohol obtained gave a small amount of a formate corresponding to it (VIII) under the conditions of the reaction; in addition, part of the alcohol was transformed into 2,2-dimethyltetrahydrofuran (IX). When formates (I) and (IV) were first obtained, their formation was explained in the same manner as the formation of the primary unsaturated chlorides by the action of hydrochloric acid upon dimethyl- and methylacetylenyl-cyclopropylcarbinol, i.e., it was assumed that first the substitution of a hydroxyl group of the cyclopropyl alcohol by a formate residue occurred, or by an atom of the halogen, then the movement of these functional groups into the β-position, and the opening of the ring.

However, the discovery of the unsaturated primary alcohol in the reaction products, required the abandonment of such an interpretation of the reaction mechanism because, first, primary alcohols esterify more readily than tertiary, and second, the formate residue does not rearrange as easily as a chlorine atom; upon boiling, the formate of the unsaturated alcohol obtained, the hydrolysis product was an unsaturated alcohol and not dicyclopropylcarbinol; the shift of the formate residue to the γ-position and the formation of the starting cyclic alcohol did not occur, whereas unsaturated primary chlorides give the starting cyclic alcohols upon hydrolysis, In addition, upon heating alcohol (VII) with formic acid, part of it was actually converted into the ester corresponding to it.

The determination of the mechanism of formation of formate during the reaction of tertiary cyclic alcohol with formic acid made possible the correct explanation of the mechanism of Rupe's [4] reaction of dimethylacetylenylcarbinol with formic acid which resulted in the formation of dimethylacrolein. Rupe explained this reaction by the consecutive hydration and dehydration of the acetylenic alcohol.

When the acetylene-allene-dienic rearrangement of chlorides formed by the action of hydrochloric acid upon dimethylacetylenylcarbinol was first studied [5], it was suggested that the formation of dimethylacrolein during Rupe reactions occurred as a result of a similar rearrangement.

Now it is considered that this reaction can be explained more simply: under the influence of formic acid, a shift of the hydroxyl group of the acetylenic alcohol to the β-position occurs, with the formation of an allenic hydroxyl derivative, which then isomerizes into dimethylacrolein.

One of the main producrs of the reaction of dimethylcyclopropylcarbinol with formic acid was 2,2-dimethyltetrahydrofuran, which was obtained by N. D. Zelinsky [6] by the action of oxalic acid upon dimethylcyclopropylcarbinol. He explained its formation by means of an intermediate product, a saturated γ-glycol (X).

It was shown by the authors that the source of the formation of γ-oxide was the unsaturated primary alcohol (VII). This alcohol vacuum distills without decomposition; upon distillation at ordinary pressure and in the presence of even minute amounts of acids, it isomerizes into the tetrahydrofuran derivative (IX).

The question of the cyclization of various compounds into tetrahydrofuran derivatives was the subject of many investigations. In more recent investigations, the conversion of γ- and δ-glycols into derivatives of tetrahydrofuran and pyran [7-14] by heating with sulfuric acid of various concentration was studied. The first investigators studying the formation of derivatives of tetrahydrofuran and pyran by the cyclization of the corresponding unsaturated alcohols in acidic media, considered that they occurred by means of an intermediately-formed glycol or halohydrin. Such a view was held by N. D. Zelinsky [6] as an explanation of the formation of dimethyltetrahydrofuran from dimethylcyclopropylcarbinol by the action of oxalic acid. Paul [15, 16] who obtained 2-methyltetrahydrofuran by the distillation of the γ-ethylenic alcohol, penten-4-ol in the presence of a small amount of concentrated sulfuric acid, suggested that the mechanism of this transformation consisted of the direct addition of the hydroxyl to the double bond, but later considered that the reaction proceeded cationotropically.

However, he believed that such a mechanism is possible only in the case of alcohols containing an end methylene group. In the rest of the cases, he considered that the reaction occurred according to Rupe's mechanism [14]. Colonge holds an analogous view on the mechanism of this reaction [17].

The authors believe that this interpretation of the mechanism of this reaction is incorrect. It was shown that 2-methylpenten-2-ol-5 converts into 2,2-dimethyltetrahydrofuran by distillation with traces of acids; the reaction, therefore, takes place in the complete absence of water, and for this reason it is rather impossible to accept a mechanism for the formation of dimethyltetrahydrofuran by means of an intermediate formation of a glycol. On this basis, it is considered that in all of the various cases, the formation of cyclic derivatives from alcohols occurs directly, and not by means of a complex course of hydration and dehydration.

I. N. Nazarov [18] believes that the cyclization reaction proceeds by means of the formation of carbonium and oxonium ions.

It is possible that in all of the above cases the reaction proceeds during cyclization by means of such a mechanism, or by means of the shifting of the hydrogen from the hydroxyl group to the β-positions.

2-Methylpentene-2-ol-5 was able to hydrate and give the glycol (X) under the conditions of heating with formic acid, whose formation was suggested by N. D. Zelinsky, and which was actually found by the authors among the reaction products.

The hydration of the double bond of the unsaturated alcohol seems more probable since the reaction conditions were sufficiently mild, and not one case of the addition of any reactant to the position of the rupture of the three-membered ring has been found. Even under more forcing conditions, during heating of methylphenylcyclopropylcarbinol with 80% formic acid, the hydrocarbon phenylcyclopropylethylene (V) was found among the reaction products, in which the trimethylene ring was stable under the conditions of the reaction and did not hydrate; it is opened under these conditions only by an isomeric transformation as a result of an unusual allylic rearrangement. Glycol (X) and the primary monoester corresponding to it were isolated, the products of the reaction of dimethylcyclopropylcarbinol with small amounts of formic acid.

In order to determine the properties of this glycol, it was synthesized from acetopropyl alcohol and ethyl magnesium bromide. Its constants corresponded sufficiently well with those of the glycol isolated from the reaction products and with the literature data [8]. It was found that if this glycol was heated with 50% formic acid to 60-70°, it was converted into the monoester; if it was heated with this acid to boiling then, in addition to the ester, derivatives of tetrahydrofuran were also formed. The glycol isolated was a primary tertiary γ-glycol; in view of the fact that tertiary alcohols esterify less readily, it could be thought that the monoester formed during the reaction with formic acid was primary, which indeed was proved by the fact that this ester gave a positive reaction for the tertiary hydroxyl [19]. The glycol was formed by the hydrolysis of this ester. The ester vacuum distils without decomposition; upon distillation at ordinary pressures, it eliminates formic acid.

The structure of the primary unsaturated alcohol (VII) was not determined, as its constants coincided with those given by Van Aerde [20]. The structure of its ester was proved by hydrolysis in alkaline medium, which resulted in the isolation of alcohol (VII); in addition, since the isomeric transformations were possible under these conditions of hydrolysis, the alcohol was also obtained by the action of an organo magnesium compound upon the ester. Acetone was obtained upon oxidation of the ester; acrylic acid was obtained in a mixture with large amounts of formic acid, from which it could not be purified. The structure of 2,2-dimethyltetrahydrofuran was proved by its oxidation with $KMnO_4$ solution; the oxidation proceeded slowly but, nevertheless, went to completion at room temperature. The only product of the oxidation was the lactone of γ-hydroxycaproic acid, which was then converted to the silver salt.

Parallel with the reaction of dimethylcyclopropylcarbinol with formic acid, reaction of formic acid with another tertiary alcohol $C_6H_{12}O$, namely, dimethylallylcarbinol, was studied. As the authors, along with Sh. A. Fridman [21], showed, methylethylallylcarbinol isomerized, by the action of H_2SO_4 into the primary alcohol, 3-methylhexene-3-ol-6. If anaologous transformation had occurred in this case, then 2-methylpentene-2-ol-5 should have been obtained, which then would have given 2,2-dimethyltetrahydrofuran.

However, this isomerization did not occur in experiments conducted under various conditions. If the reaction was conducted heating with acid diluted 1:1, or with concentrated acid at 0°, then dimethylallylcarbinol was recovered unchanged; only small amounts of dehydration products were formed. On heating dimethylallylcarbinol with concentrated HCOOH, the dehydration proceeded more completely, and condensation products were formed. A substance was isolated from the mixture of products, which must be accepted as the trimer of the hydrocarbon C_6H_{10} on the basis of analytical results. The product obtained did not decolorize a $KMnO_4$ solution, and did not add bromine from a chloroform solution. Apparently, a product of cyclic structure was formed as a result of polymerization, which did not contain double bonds, or a side chain. The structure of the hydrocarbon was not investigated more fully.

EXPERIMENTAL

Synthesis of Dimethylcyclopropylcarbinol.

The starting acetyltrimethylene was obtained from acetopropyl alcohol. Acetopropyl alcohol was converted into the bromide by distillation with a two-fold quantity of hydrobromic acid with b.p. 118-124°. The alcohol was added through a dropping funnel to the boiling acid in small portions, corresponding to the distillation of the bromide. The bromide distilled was separated from the water and used directly in the reaction. The yield of the crude product was 75-80%. Powdered alkali, (KOH or NaOH), in a quantity slightly greater than the theoretical, was added with efficient shaking and mixing to the bromide which had been placed into a round-bottom flask and left to stand overnight. On the following day, the contents of the flask were dissolved in water, and the acetyltrimethylene steam distilled, salted out with potassium carbonate, dried, and distilled. B.p. 109-112°. Yield, 75% based on the crude bromide.

Dimethylcyclopropylcarbinol was obtained from methyl magnesium bromide and acetyltrimethylene. The product obtained, with b.p. 118-125° (68-70%), very rapidly decolorized a $KMnO_4$ solution. For this reason, it was oxidized with $KMnO_4$ to remove the unsaturated impurities. The yield of the pure product was 54-55%.

B.p. 120-123°; d_4^{20} 0.888; d_4^0 0.9053; n_D^{20} 1.4323; MR_D 29.21. $C_6H_{12}O$. Calculated: MR_D 29.79.

The constants obtained corresponded to the literature data [5].

Reaction of Dimethylcyclopropylcarbinol with Boiling Formic Acid.

150 g of dimethylcyclopropylcarbinol was heated to boiling for 1.5 hours with 300 ml of formic acid (dilute 1:1, pH 0.44, or ~55%). After neutralization of the unreacted acid with dry sodium carbonate, the reaction products were extracted with ether.

After drying and removal of the solvent, the residue was distilled at ordinary pressure and then in vacuum. The following fractions were isolated after several redistillations: 1) 90-92° – 28.8 g (19.2%). 2) 108-112° – 6.2 g (5%). 3) 119-125° – 4.0 g (5%). 4) 152-155° – 35.5 g. 5) 97.5-98.5° at 7 mm – 18.9 g (8.6%). 6) 117-118° at 13 mm – 5.5 g (3%).

In addition, intermediate fractions were obtained. Fraction 3, 119-125°, was the starting dimethylcyclopropylcarbinol.

Investigation of the fraction with b.p. 90-92°; d_4^{20} 0.8477; n_D^{20} 1.4901; MR_D 29.18 $C_6H_{12}O$. Calculated MR_D 29.35.

0.1207 g substance: 0.3005 g CO_2; 0.1141 g H_2O. Found %: C 71.82; H 11.82. $C_6H_{12}O$. Calculated %: C 72.9; H 12.0.

The substance slowly decolorized a $KMnO_4$ solution and did not give reactions for hydroxyl or carbonyl groups, which meant that it must be 2,2-dimethyltetrahydrofuran.

Oxidation. 5 g of the substance was oxidized for 2 days. The MnO_2 residue was filtered and washed with hot water, the filtrate was evaporated to a small volume, and acidified with sulfuric acid, whereupon oil droplets floated on the surface. The oxidation products were extracted with ether. After drying with Na_2SO_4 and removal of the solvent, a substance with b.p. 203-204°, the lactone of γ-hydroxyisocaproic acid, was obtained.

For the determination of the neutralization equivalent, the lactone was boiled with alkali, and the excess of the latter was titrated with hydrochloric acid.

0.1788 g substance: 42 ml NaOH (T 0.7456); 14.4 ml HCl (T 1.083). Found: E 113.7. $C_6H_{10}O_2$. Calc'd: E 114.0.

For the preparation of the silver salt of γ-hydroxyisocaproic acid, the lactone was dissolved in ammonia with heating on the water bath. The excess ammonia was removed by evaporation. A concentrated solution of $AgNO_3$ was added to the solution of the ammonium salt obtained. The precipitated silver salt was filtered, washed with water, and dried in a desiccator.

0.1133 g substance: 0.0511 g Ag. Found %: Ag 45.10. $C_6H_{11}O_3Ag$. Calculated %: Ag 45.19

Investigation of the fraction with b.p. 108-112°. The substance gave a voluminous precipitate with 2,4-dinitrophenylhydrazine; the 2,4-dinitrophenylhydrazone melted at 145-146°; a mixed melting point with authentic acetyltrimethylene gave no depression. The dimethylcyclopropylcarbinol, used for the reaction with formic acid, was initially tested for acetyltrimethylene by means of 2,4-dinitrophenylhydrazine, and gave no precipitate with it. In order to conclusively determine whether or not acetyltrimethylene was present in the dimethylcyclopropylcarbinol, ultraviolet absorption spectra of both of these substances were made. For acetyltrimethylene, the character of the absorption curve coincided with that reported in the literature. A maximum at 270 mμ was found in the absorption spectrum of the alcohol, which indicated the presence of a carbonyl group in the compound. Therefore, acetyltrimethylene was present in the starting dimethylcyclopropylcarbinol. It could be isolated by distillation, when the concentration of the alcohol decreased as a result of the reaction with formic acid. Therefore, acetyltrimethylene with 108-112° which was isolated, was not a product of the reaction between dimethylcyclopropylcarbinol and formic acid.

Investigation of the fraction with b.p. 152-155°. As shown by the investigation, this fraction was not an individual substance but a mixture of two products with close boiling points: the primary alcohol, 2-methylpentene-2-ol-5 and its formate. The constants of the fraction with b.p. 152-155°, isolated in several experiments, differed from each other, and apparently depended on the ratio of the components present.

d_4^{20} 0.9028, 0.9105, 0.9098; n_D^{20} 1.4364, 1.4340, 1.4340. On conversion to $C_7H_{12}O_2$. Found: MR_D 37.09, 36.60, 36.66. On conversion to $C_6H_{12}O$. Found: MR_D 28.97, 28.61, 28.63. $C_7H_{12}O_2F$. Calculated: MR_D 35.91. $C_6H_{12}OF$. Calculated: MR_D 31.09.

A determination of the number of hydroxyl groups gave results which indicated the presence of 30-35% of the alcohol in the mixture. In order to show the presence of the ester in the mixture, the fraction 152-155° was subjected to hydrolysis.

20 g of the substance was heated with stirring with a two-fold quantity of 10% K_2CO_3 solution for 8-10 hours. After extraction with ether, drying, removal of the solvent, and distillation, a fraction with b.p. 156-157° was obtained in a yield of about 80%. Its constants: d_4^{20} 0.8556; n_D^{20} 1.4464; MR_D 31.20. $C_6H_{12}OF$ Calculated: MR_D 31.09. Literature data for 2-methylpentene-2-ol-5: b.p. 157°; d_4^{20} 0.8577, 0.8549; n_D^{20} 1.4456, 1.4454.

0.0913 g substance: 0.2408 g CO_2; 0.0972 g H_2O. 0.1387 g substance: 33.0 ml CH_4 (13.5°, 761 mm). Found %: C 71, 93, H 11.91. OH number 0.997. $C_6H_{12}OF$ Calculated %: C 72.0; H 12.0. OH number 1.

Therefore, only one product known in the literature, 2-methylpentene-2-ol-5, was obtained as a result of the hydrolysis of the fraction with b.p. 152-155°;

The aqueous solution remaining after the extraction of the alcohol was acidified with sulfuric acid. The volatile acids were steam distilled. A qualitative test with a mercuric chloride solution showed the presence of formic acid. The distilled solution of the volatile acids was titrated with NaOH; the amount of acid titrated showed that the fraction with b.p. 152-155° contained about 65% of the formate.

Investigation of the fraction with b.p. 97.5-98.5° at 7 mm. Upon attempting to distill the product at ordinary pressure, the formation of a noticeable amount of formic acid was noticed, whose presence was established by a qualitative reaction with mercuric chloride. The analytical results obtained showed that the fraction with b.p. 97.5-98.5° at 7 mm had the formula $C_7H_{14}O_3$ and was the monoester of α,α-dimethyltetramethylene glycol and formic acid.

d_4^{20} 1.0123; d_4^0 1.0256; n_D^{20} 1.4395; MR_D 37.97. $C_7H_{14}O_3$. Calculated: MR_D 37.71.
0.1263 g substance: 0.2652 g CO_2; 0.1083 g H_2O. 0.865 g substance: 14.4 ml CH_4 (16.5°, 757 mm). 0.1083 g substance: 15.09 g benzene: Δt 0.25°. Found %: C 57.34; H 9.67; OH number 1.001; M 141. $C_7H_{14}O_3$. Calculated %: C 57.51; H 9.65; OH number 1. M 142.

5 g of the fraction with b.p. 97.5-98.5° at 7 mm was hydrolyzed by heating and stirring with a two-fold quantity of 10% potassium carbonate solution for 1 day. After extraction with ether, drying, and removal of the solvent, the residue was vacuum distilled. One product with b.p. 112-113° at 12 mm was obtained.

d_4^{20} 0.9789; n_D^{20} 1.4560; MR_D 32.30. $C_6H_{14}O_2$. Calculated: MR_D 32.65.
0.0939 g substance: 38 5 ml CH_4 (16°, 757.8 mm). OH number 1.99. $C_6H_{14}O_2$. Calculated: OH number 2.

The constants of the substance obtained coincided with those of dimethyltetramethylene glycol synthesized by the authors.

The aqueous layer after the extraction of the glycol was acidified with sulfuric acid, and the volatile acids were steam distilled. Formic acid was detected in the distillate. In order to establish the position of the hydroxyl group in the ester, the qualitative Denigés [19] reaction was tried, and a voluminous yellow precipitate with mercuric oxide and sulfuric acid, characteristic for tertiary alcoholic groups, was obtained.

Investigation of the fraction with b.p. 117-118° at 13 mm.

d_4^{20} 0.9786; n_D^{20} 1.4557; MR_D 32.76. $C_6H_{14}O_2$. Calculated: MR_D 32.96.
0.0893 g substance: 0.2008 g CO_2; 0.0920 g H_2O. 0.0936 g substance: 36.9 ml CH_4 (13.5°, 752 mm). Found %: C 61.32; H 11.52; OH number 1.93. $C_6H_{14}O_2$. Calculated %: C 61.01; H 11.86; OH number 2.

The substance obtained corresponds to α,α-dimethyltetramethylene glycol [8].

Reaction of α,α-Dimethyltetramethyleneglycol with Formic Acid.

The glycol was prepared from methyl magnesium bromide and acetopropyl alcohol with a yield of about 40%. d_4^{20} 0.9817; d_0^0 0.9858; n_4^{20} 1.4560; MR_D 32.67.

Experiment I. 10 g of the glycol and 13 ml of formic acid, diluted 1:1, were heating to boiling for 1 hour, then the acid was neutralized with dry sodium carbonate, and the reaction products were extracted with ether. After drying and removal of the ether, the residue was distilled, resulting in the isolation of: 2.4 g (28%) of a substance with b.p. 90-93° (2,2-dimethyltetrahydrofuran); 2 g of a fraction with b.p. 103-106° at 13 mm (16%) corresponding to the slightly impure monoester of the glycol, and 2.1 g of a fraction with b.p. 106-120° at 13 mm, a mixture of the ester and the starting glycol.

Experiment II. The glycol and the acid were heated on the water bath to 60-70° for 3 hours. The pure monoester of the glycol with b.p. 97-98° at 7 mm, 11.1 g (30%), a mixture of the glycol and ester with b.p. 98-112° at 7 mm, 8.5 g, and the starting glycol with b.p. 112-114° at 7 mm, 4.0 g (12%) were obtained.

Therefore, at 60-70° the formation of the oxide from the glycol does not occur; only the esterification of the glycol occurs.

Reaction of 2-Methylpentene-2-ol-5 and Its Ester with Formic Acid.

20.1 g of the mixture of the alcohol and ester was heated to boiling for 2.5 hours with 22 ml of HCOOH, diluted 1:1 (pH 0.44). After neutralization of the acid with dry sodium carbonate, the reaction products were extracted with ether. After drying, removal of the solvent, and distillation, the following fractions were obtained: 1) 90-93° – 9.55 g (47.5%), 2) 93-152° – 0.5 g, 3) 152-153° – 0.5 g (starting product).

The constants of the substance with b.p. 90-93° coincided with those obtained for 2,2-dimethyltetrahydrofuran.

Reaction of Dimethylcyclopropylcarbinol with Formic Acid at 60-70°.

37 g of the alcohol was heated with 80 ml of formic acid (pH 0.44) for 1.5 hours at 60-70°. After usual processing of the reaction products and distillation, at first in vacuum and then at ordinary pressure, a mixture of the unsaturated alcohol and its formate with b.p. 152-155°, 20.1 g (54%) was isolated as the main product. In addition, small amounts of acetyltrimethylene (0.8 g) and the starting alcohol (0.5 g) were also isolated. No tetrahydrofuran derivatives were formed at these reaction temperatures.

Reaction of Dimethylallylcarbinol with Formic Acid.

Dimethylallylcarbinol was obtained according to R. Ya Levina's method [22] from allyl chloride, magnesium, and acetone. 54 g of the alcohol with b.p. 116-118° (yield 54%) was obtained.

Experiment I. 12 g of the alcohol was boiled for 1.5 hours with HCOOH (1:1) (pH 0.44). As a result, 51% of the alcohol (6.1 g) was recovered; in addition 1.9 g of a fraction with b.p. 48-115° was obtained, from which a fraction with b.p. 70-82° was isolated, corresponding to a mixture of hydrocarbons obtained by the dehydration of dimethylallylcarbinol [21].

Experiment II. 40 g of dimethylallylcarbinol was stirred for 6 hours with concentrated HCOOH at 0°. As a result, unchanged dimethylallylcarbinol was recovered and about 1 g of hydrocarbons with b.p. 70-82° was isolated.

Experiment III. 44 g of the alcohol was boiled for 1.5 hours with concentrated HCOOH. The acid was neutralized with dry sodium carbonate. After extraction with ether, and distillation in vacuum, a substance with b.p. 142-143° at 12 mm, 87.3 g quantity, was obtained as the main product. The product did not decolorize a $KMnO_4$ solution, and the separation of HBr occurred upon the action of a bromine solution in chloroform. The results of elementary analysis showed that the substance was a hydrocarbon whose molecular weight corresponded to a trimer.

d^{18}_4 0.8689; n^{18}_D 1.4905; MR_D 81.92. $C_{18}H_{30}F_2$. Calculated: MR_D 81.01
0.1071 g substance: 0.3421 g CO_2; 0.1198 g H_2O. 0.1515 g substance: 12.05 g benzene: Δt 0.26°
Found %: C 87.11; H 12.51; M 248.0. $C_{18}H_{30}$. Calculated %: C 87.80; H 12.20; M 246.

SUMMARY

1. The reaction of dimethylcyclopropylcarbinol with formic acid was studied

2. A mechanism for this reaction is given.

3. It was shown that, initially, the isomerization of dimethylcyclopropylcarbinol into the unsaturated primary alcohol, 2-methylpentene-2-ol-5, occurred by means of the shift of the hydroxyl to the β-position and the opening of the three-membered ring.

4. It was shown that the unsaturated alcohol partly formed the formate, and was partly isomerized to 2,2-dimethyltetrahydrofuran.

5. In addition to the above products, 2,2-dimethyltetramethylene glycol and the half ester of the glycol and formic acid were also isolated from the reaction products.

6. 2-Methylpentene-2-ol-5 was obtained upon hydrolysis of the ester of the unsaturated alcohol. The cyclic alcohol did not form.

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Awarded the Order of Lenin.
The A. E. Favorsky Laboratory.

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* See Consultants Bureau English translation, page 891.

** See Consultants Bureau English translation, page 437.

TRANSFORMATIONS OF ACETYLENIC ALCOHOLS

CONTAINING POLYMETHYLENE RINGS

II. 1-PHENYLACETYLENYLCYCLOHEXANOL-1

E. D. Venus-Danilova, M. V. Gorelik, and T. A. Nikolaeva

Recently one of the authors together with M. V. Gorelik [1] showed that 1-phenylacetylenylcyclopentanol-1 was transformed into the isomeric ethylenic ketone, cyclopentylideneacetophenone, in the presence of mercuric sulfate in acidic medium.

In order to determine to what extent an analogous reaction would occur for other tertiary polymethylene alcohols with acetylenic radicals, the behavior of 1-phenylacetylenylcyclohexanol-1 in an acidic solution of mercuric sulfate under the above conditions was studied.

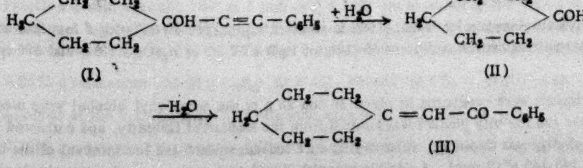
1-Phenylacetylenylcyclohexanol-1 was first synthesized by Zh. I. Iotsich [2], and then later by foreign chemists [3] who dehydrated this alcohol with potassium bisulfate to prepare 1-phenylacetylenylcyclohexene-1.

On heating 1-phenylacetylenylcyclohexanol-1 at 60-65° with mercuric sulfate in the presence of dilute sulfuric acid (conditions completely analogous to those reported in Communication I [1]), only the unsaturated ketone, cyclohexylideneacetophenone (III) was obtained. Neither α- or β-ketoalcohols, nor unsaturated ketones with a double bond in the polymethylene ring [4, 5] were detected in this case.

The mechanism of the transformation of 1-phenylacetylenyloyclopentanol-1 into cyclopentylideneacetophenone [1] remained open. The unsaturated ketone could have formed by the isomerization of the acetylenyl alcohol with a shift of the hydroxyl group into the β-position, or as a result of the elimination of water from the product of the hydration of the acetylenic alcohol, the β-ketol.

In order to solve this problem, the action of a more dilute mercuric sulfate, as well as various concentrations of sulfuric acid itself upon 1-phenylacetylenylcyclohexanol-1 were studied. It was found that a mixture of the unsaturated ketone and a hydroxyl-containing product was obtained under milder hydration conditions. This mixture was completely converted into cyclohexylideneacetophenone by treatment with sulfuric acid. In addition, it was shown that the acetylenyl alcohol was not converted into the ethylenic ketone by the action of sulfuric acid (15 and 30%), i.e., it did not undergo the acetylene-allene rearrangement.

Therefore, the unsaturated ketone (III) was obtained as a result of the hydration of the acetylenic alcohol (I) at the triple bond, and the subsequent dehydration of the β-ketol (II) formed as a result of the first reaction.



The dehydration is aided by the presence of the very active methylene group hydrogens in the chain of the molecule of the keto alcohol. The phenomenon was observed previously during the hydration of 3-phenylpropyn-2-ol-1 and 4,4-dimethylpentyne-2-ol-1, which finally formed unsaturated ketones with small amounts of the corresponding β-keto alcohols [6].

Upon comparison of the many literature reports on the hydration of tertiary acetylenic alcohols of the type $RR_1COH-C\equiv CH$ in acidic media in the presence of mercuric sulfate, the following fact stands out: normal reaction products, α-ketoalcohols ($RR_1COH-CO-CH_3$), are formed with the presence of aliphatic radicals (R and R_1 = alkyl) in these alcohols [7-12].

In the above case, because of the resemblance of polymethylene alcohols to the aliphatic, neither 1-phenylacetylenylcyclopentanol-1, nor 1-phenylacetylenylcyclohexanol-1 isomerize directly into ethylenic ketones by the action of an acidic mercuric sulfate solution, or in the presence of sulfuric acid alone. The presence of these ketones in the reaction products is explained by the dehydration of the β-ketoalcohol.

If one of the aliphatic radicals is substituted by an aryl, in addition to the hydration of the alcohol, an acetylene-allene rearrangement leading to the isomeric products, the unsaturated aldehydes, readily occurs [13]. The isomerization of purely aromatic tertiary acetylenic alcohols into unsaturated ketones by the action of sulfuric acid [14], or other acidic catalysts, is also reported in the literature [15].

Similar effects of the aromatic radicals on the acetylene-allene rearrangement were found by one of the authors during a study of the transformations of acetylenic pinacols of the type $RR_1COH-COH(R_2)C\equiv CR_3$ by the action of sulfuric acid. In the case where R_2 = aryl, the reaction products were found to be ethylenic γ-ketoalcohols (products of the acetylene-allene rearrangement), or the products of their further transformations [16-18]; where R_2 = alkyl, the acetylene-allene rearrangement either did not take place at all [19], or was not the main direction of the reaction [20].

Of course, the structure of the molecule as a whole, the character of all the radicals, and their mutual distribution must be considered under identical conditions during an examination of the transformations.

Ultraviolet absorption spectra were made of cyclohexylideneacetophenone, cyclopentylideneacetophenone, reported in the previous communication [1], and for comparison, that of acetophenone. The absorption spectra were photographed in a quartz ISP-22 spectrograph. The absorption curves are given in the Figure.

The clear resemblance of curves I and II corresponding to cyclopentylidene- and cyclohexylideneacetophenone is apparent as well as their difference from curve III, corresponding to acetophenone. There are three general regions of absorption in the spectra of all three compounds: from 2400-2600, from 2600-2800, and 3000-3800 A. The absorption spectra of cyclopentylidene- and cyclohexylideneacetophenone have greater absorption coefficients in comparison to acetophenone, and shifts of the main maxima of 20-30 A toward the longer wavelengths.

The presence of an ethylenic bond was proved by means of infra-red absorption spectra on a Hilger D-88 spectrometer. The characteristic frequency band for the C = C bond lies in the region of 10.5 μ.

The spectrophotographic investigations were conducted in the Roentgeonographic Laboratory of the Leningrad Institute of Technology under the direction of O. N. Setkina, whom the authors wish to thank for her aid and advice.

EXPERIMENTAL

1-Phenylacetylenylcyclohexanol-1 was prepared according to Zh. I. Iotsich's* method. The purification of the alcohol was effected according to a previously reported method [1], i.e., solution of the substance in the minimum amount of methyl alcohol and precipitation with large excess of cold water. After two such purifications, long scale-like crystals with m.p. 61-62° were obtained, as reported in the literature [2, 3]. Yield, 36 g or 48% of the theoretical amount.

Experiment I. 1-Phenylacetylenylcyclohexanol-1 was heated for 2.5 hours to 60-65° with a four-fold excess of an aqueous solution of mercuric sulfate in sulfuric acid (10 g of HgO + 50 ml of H_2SO_4 d 1.84, and 300 ml of H_2O) [11].

Two analogous experiments were conducted in which 10 and 25 g of the acetylenyl alcohol were used. After heating, the mixture of water and the oily product was filtered from the suspended turbidity, and extracted 2 times with benzene, in which the turbidity was insoluble. After drying with sodium sulfate and the removal of the benzene, the residue was distilled at 140-140.5° (2 mm). A slightly greenish liquid with a pleasant odor was obtained, which immediately decolorized an aqueous potassium permanganate solution and a solution of bromine in chloroform, but which did not form methane upon reaction with methyl magnesium iodide. Yield, 80% of the theoretical amount.

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*G. A. Davydov participated in the synthesis of the alcohol.

d_0^0 1.0577; d_{20}^{20} 1.0436; d_4^{20} 1.0418; n_D^{20} 1.5786. Found: MR_D 61.77. $C_{14}H_{16}OF_4$. Calculated: MR_D 60.61.

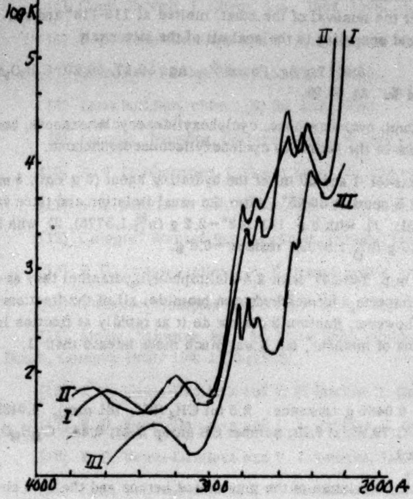
0.1407 g substance: 0.4328 g CO_2; 0.1040 g H_2O. 0.2667 g substance: 11.48 g C_6H_6: Δt 0.6°. Found %: C 83.89; H 8.21; M 193.8. $C_{14}H_{16}O$. Calculated %: C 84.00; H 8.00; M 200.

The substance formed an orange precipitate at once with 2,4-dinitrophenylhydrazine, which showed a pyrazoline reaction. After recrystallization from boiling ethyl alcohol with the addition of ethyl acetate, the pyrazoline melted at 146-147°.

0.1203 g substance: 14.3 ml N_2 (12°, 779 mm). 0.1002 g substance: 0.2313 g CO_2; 0.0487 g H_2O. Found %: C 62.95; H 5.40; N 14.61. $C_{20}H_{20}O_4N_4$. Calculated %: C 63.17; H 5.26; N 14.74.

Twenty-four hours later, the substance with b.p. 140-140.5° at 2 mm solidified into a uniform white mass. After pressing on a porous plate and recrystallization from alcohol, the substance melted at 41-42° and gave the same pyrazoline (m.p. 146-147°) with 2,4-dinitrophenylhydrazine, as the liquid product with b.p. 140-140.5° at 2 mm. A determination of the molecular weight of the crystalline substance showed that it was the monomer.

0.1053 g substance: 15.09 g C_6H_6: Δt 0.17°. Found: M 205. $C_{14}H_{16}O$. Calculated: M 200.



Ultraviolet absorption spectra in n-hexane. I) Cyclopentylideneacetophenone, II) cyclohexylideneacetophenone, III) acetophenone.

Oxidation of the substance with m.p. 41-42°. 10 g of the unsaturated ketone and 8.0 g of potassium permanganate were used (theory: 7.9 g of the oxidizing agent based on two moles of potassium permanganate per mole of the ketone); 300 ml of a 1% solution of potassium permanganate was added to the ketone with efficient stirring and the remaining 5 g of the oxidizing agent was added in dry form according to the decolorization of the solution. The oxidation proceeded without any external heating with a slight evolution of heat, and was finished within 2.5 hours. The manganese dioxide was filtered, washed with hot water, then ether, and an ether extraction of the filtrate was made. After the removal of the ether, 5.1 g of a light yellow liquid with a pleasant odor was obtained. A substance with b.p. 155° was obtained as the main fraction (1.8 g) upon distillation at ordinary pressure; upon further distillation a rapid rise of the temperature to 220° and a partial decomposition occurred. For this reason, the residue was distilled at 5 mm; b.p. 128-130°, 2.0 g. There was 4 g of a tar in the residue.

Fraction 1 with b.p. 155° at ordinary pressure formed a semicarbazone with m.p. 165-166° and a 2,4-dinitrophenylhydrazone with m.p. 160-162° corresponding to cyclohexanone [21] (mixed melting point).

Fraction 2 with b.p. 128-130° at 5 mm (n_D^{20} 1.449) was a yellow liquid with a pleasant camphor-like odor, not containing a hydroxyl, decolorizing potassium permanganate and bromine, forming a semicarbazone (in alkaline medium) with m.p. 175+5-177° and a 2,4-dinitrophenylhydrazone with m.p. 129-130°.

0.2071 g substance: 12.31 g C_6H_6: Δt 0.49°. Found: M 172. $C_{12}H_{18}O_2$. Calculated: M 178.

Analysis of the 2,4-dinitrophenylhydrazone with m.p. 129-130°.

0.1066 g substance: 14.4 ml N_2 (16°, 701 mm). Found %: N 15.73. $C_{18}H_{22}O_4N_4$. Calculated %: N 15.64.

According to properties and analysis of the 2,4-dinitrophenylhydrazone, the substance with b.p. 128-130° at 5 mm is cyclohexylidenecylcohexanone [22] formed as the result of a ketol condensation of cyclohexanone.

3.5 g of a precipitate (m.p. 99-105°) was formed by the acidification of the organic acid salts with dilute sulfuric acid. Benzoic acid with m.p. 120-121° was obtained by sublimation of the precipitate. After many washings of the precipitate with water, benzoylformic acid was detected in the washings, which formed a difficultly water-soluble yellow phenylhydrazone with m.p. 152-153° (mixed melting point with authentic benzoylformic acid phenylhydrazone [23]). The aqueous solution in which benzoylformic acid was also detected, was subjected to steam distillation in order to decompose the benzoylformic acid and remove the formic; the residue was continually extracted with ether. The residue obtained after the removal of the ether, melted at 110-118° and consisted of benzoic acid with a small impurity of adipic acid according to the analysis of the silver salt.

0.0901 g salt. 0.0452 g Ag. 0.1030 g salt. 0.0517 g Ag. Found %: Ag. 50.17, 50.20. $C_7H_5O_2Ag$. Calculated %: Ag. 47.12. $C_6H_8O_4Ag_2$. Calculated %: Ag 59.96.

The products of the oxidation of the ethylenic ketone, cyclohexanone, cyclohexylidenecyclohexanone, benzoic acid, and benzoylformic acid confirmed the structure of the ketone as cyclohexylideneacetophenone.

Experiment II. 15 g of 1-phenylacetylenylcyclohexanol-1 and 60 ml of the hydrating agent (5 g HgO, 5 ml of H_2SO_4 d 1.84, and 200 ml of H_2O)* were heated for 2.5 hours at 60-65°. After the usual isolation and three vacuum distillations at 2 mm, three fractions were obtained: 1) with b.p. 141-143°—2.2 g (n_D^{20} 1.5775), 2) with b.p. 143-154°—5.6 g (n_D^{20} 1.5750), 3) with b.p. 154-157°—5.3 g (n_D^{20} 1.5700); residue—0.5 g.

All three fractions gave the same pyrazoline with m.p. 146-147° with 2,4-dinitrophenylhydrazine; they decolorized a solution of bromine in chloroform, whereby fraction 3 formed hydrogen bromide; all of the fractions decolorized an aqueous potassium permanganate solution, however, fraction 3 did not do it as rapidly as fraction 1; all reacted with methyl magnesium iodide with the formation of methane, but 3 was much more intense than 1.

Analysis of fraction 3 with b.p. 154-157° at 2 mm.

0.1038 g substance: 0.3044 g CO_2; 0.0759 g H_2O. 0.0465 g substance: 2.5 ml CH_4 (21°, 761 mm). 0.0439 g substance: 2.2 ml CH_4 (21°, 761 mm). Found %: C 79.98; H 8.12; number OH group 0.48, 0.44. $C_{14}H_{16}O$. Calculated %: C 77.06; H 8.26; number OH group 1.

The analytical results and the properties showed that a mixture of the unsaturated ketone and the keto alcohol was obtained in this case.

All of the three fractions were combined, 10 g quantity and treated with 15% sulfuric acid at 65-70° for 2 hours; 8.6 g of a substance with b.p. 142-143° at 3 mm and m.p. 41-42° was isolated, which corresponded to cyclohexylideneacetophenone.

Experiment III. 10 g of the acetylenic alcohol with m.p. 61-62° was heated for 2.5 hours to 65-70° with 200 ml of 15% sulfuric acid. After the usual isolation, 9.2 g of a thick liquid was obtained which rapidly crystallized. The substance reacted violently with methyl magnesium iodide with the formation of methane, and did not form a precipitate with a solution of 2,4-dinitrophenylhydrazine. After purification by means of reprecipitation by water from a methyl alcohol solution, the substance was isolated in the form of characteristic thin crystals with m.p. 61-62°, and was the starting acetylenic alcohol.

By the action of 30% sulfuric acid on 1-phenylacetylenylcyclohexanol-1 with heating up to 80° for 3 hours, the acetylenic alcohol was also unchanged.

SUMMARY

1. It was shown that 1-phenylacetylenylcyclohexanol-1 formed the isomeric ketone, cyclohexylideneacetophenone, by the action of mercuric sulfate in the presence of 8% free sulfuric acid, and a mixture of the unsaturated ketone and β-ketoalcohol by the action of that salt with 3% sulfuric acid.

2. It was shown that neither 15%, nor 30% sulfuric acid, without the mercuric salt, had any effect on the acetylenic alcohol.

3. It was shown, that the ethylenic ketone, formed under the conditions of G. M. Kucherov's reaction for tertiary polymethylene acetylenic alcohols (5-and 6-membered cycles), was a secondary product of the reaction, and was obtained as a result of the removal of water from the β-ketoalcohol, product of the hydration of the acetylenic alcohols.

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* In experiment I the concentration of free sulfuric acid corresponded to about 8%; in experiment II, 3%.

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**** See Consultants Bureau English translation page 1605.

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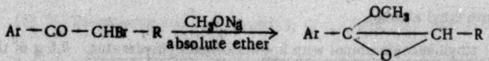
****** See Consultants Bureau English translation page 2477.

INVESTIGATIONS OF CYCLIC ACETALS OF HYDROXYCARBONYLIC COMPOUNDS

V. METHYLLACTOLIDES OF ETHYLBENZOYLCARBINOL AND METHYL-p-ANISOYLCARBINOL

T. I. Temnikova and N. I. Almashi

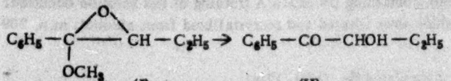
In order to further study the properties and transformations of lactolides of α-ketoalcohols, the synthesis of the methyllactolides of two ketoalcohols, ethylbenzoylcarbinol and methyl-p-anisoylcarbinol was effected during the present investigation. Both of the methyllactolides were prepared by means of a method reported in the first communication of this series [1].



Where Ar = C_6H_5; R = C_2H_5 and Ar = $CH_3OC_6H_4$, R = CH_3.

The methyllactolide of ethylbenzoylcarbinol (I) was considerably more stable than that of methylbenzoylcarbinol; however, upon distillation and storage, it slowly polymerized. The methyllactolide of methylanisoylcarbinol was very unstable, it polymerized rapidly upon standing in ether solutions in the presence of sodium methylate, upon distillation, and upon storage in pure form. Therefore, the introduction of a CH_3O- group into the para position does not change the stability of the methyllactolide of methylbenzoylcarbinol; on the other hand, the substitution of a methyl by an ethyl directly at the oxide ring considerably increased the stability of the methyllactolide during distillation, as well as upon storage.

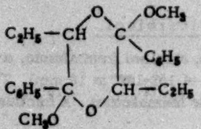
In order to prove the structure of the substance obtained by the action of sodium methylate upon α-bromoethylphenyl ketone as the methyllactide, its hydrolysis in acidic medium was conducted:



(I) (II)

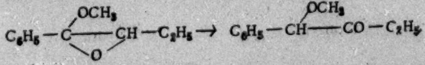
The isolated ethylbenzoylcarbinol (II) was identified and ultraviolet absorption curves of both compounds (the methyllactolide (I) and the ketoalcohol (II)) were taken. The absorption of ethylbenzoylcarbinol has maxima characteristic for benzoyl group (the Figure, Curve II) at a λ of 322 mμ, and λ 280 mμ [2]. The methyl lactolide does not have maxima in these regions, but it absorbs at the shorter wavelengths (λ 265-242 mμ) because of the presence of a benzene ring in it.

Because of the ease of hydrolysis in aqueous acidic medium, the methyllactolide of ethylbenzoylcarbinol formed the 2,4-dinitrophenylhydrazone of ethylbenzoylcarbinol by the action of a sulfuric acid solution of 2,4-dinitrophenylhydrazine. A dimerization occurred by the action of 1% HCl in methanol, and the cyclodimethyllactolide of ethylbenzoylcarbinol with m.p. 239-240° (III) was formed, which was previously reported [3].

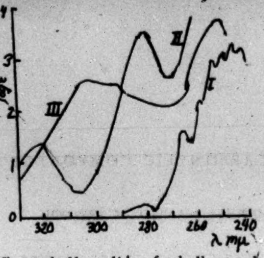


(III)

An isomerization of the methyllactolide of ethylbenzoylcarbinol into a carbonyl-containing compound (Figure, Curve III) occurred by the action of magnesium bromide etherate: in analogy with previously studied cases, it can be supposed that the isomerization occurred according to the scheme:



EXPERIMENTAL



I) Methyllactolide of ethylbenzoyl carbinol. II) ethylbenzoylcarbinol, III) methyl ether of phenylpropionylcarbinol.

I. Preparation of the Methyllactolide of Ethylbenzoylcarbinol.

38 g of α-bromoethylphenyl ketone was added dropwise to a suspension of 8 g of sodium methylate in absolute ether. The mixture was left to stand for 24 hours, the sodium bromide and the excess sodium methylate were removed by filtration. The ether solution was vacuum distilled. 18 g of a substance with b.p. 94-95° at 10 mm resulted after two distillations. Yield, 65%.

d_4^{16} 1.0256; n_α^{16} 1.49634; n_D^{16} 1.4992; n_β^{16} 1.50987; MR_α 50.76; MR_β 51.93. $C_{11}H_{14}O_2$.

Calculated MR_α 50.52; MR_β 51.65 (0.35 was added during the calculation as the increment for the oxide ring for the α line, and 0.45 for the β).

0.1349 g substance: 0.3663 g CO_2; 0.0983 g H_2O. 0.1190 g substance: 0.3244 g CO_2; 0.0858 g H_2O. 0.2060 g substance: 0.2779 g AgI. 0.0914 g substance: 15.71 g benzene: Δt 0.17°. Found %: C 74.05, 74.33; H 8.16, 8.07; OCH_3 17.8. M 176. $C_{11}H_{16}O_2$. Calculated %: C 74.11; H 7.92; OCH_3 17.4; M 178.

The substance reacted violently with ethyl alcohol.

Reaction of the Methyllactolide of ethylbenzoylcarbinol with 2,4-dinitrophenylhydrazine. 0.5 g of the methyllactolide of ethylbenzoylcarbinol was added to a solution of 0.4 g of dinitrophenylhydrazine in 3 ml of concentrated sulfuric acid in 2 ml of water and 10 ml of alcohol. The mixture was left to stand overnight. Orange crystals deposited, which were recrystallized from light petroleum ether. M.p., 174-175°.

0.1168 g substance: 16.4 ml N_2 (18°, 756 mm). Found %: N 16.81; $C_{16}H_{16}O_5N_4$. Calculated %: N 16.28.

The substance did not contain a methoxyl group.

Hydrolysis of the methyllactolide. 5 g of the methyllactolide was heated with 5% aqueous H_2SO_4 for 6 hours. The hydrolysis product distilled completely at 90° at 2 mm. A glycol with m.p. 67-68° was obtained by the action of ethyl magnesium bromide on it. A mixed sample with glycol-3-phenylhexandiol-3,4 with m.p. 67-68° melted at the same temperature [4].

Reaction of the methyllactolide with methyl alcohol containing 2% HCl 2 g of the methyllactolide was added dropwise with cooling to 20 ml of methyl alcohol containing 2% HCl. A frothing of the solution occurred; colorless crystals deposited as a result of the reaction, which were filtered and recrystallized from alcohol; m.p. 239-240°. 1.5 g was obtained.

Found %: OCH_3 17.6 $C_{20}H_{22}O_2(OCH_3)_2$. Calculated %: OCH_3 17.41.

The crystals obtained melted without depression in a mixture with the cyclodimethyldilactolide of ethylbenzoylcarbinol reported previously [3], and obtained by the action of HCl in CH_3OH on ethylbenzoylcarbinol.

Isomerization of the methyllactolide of ethylbenzoylcarbinol into the methyl ether of phenylpropionylcarbinol. 4 g of the methyllactolide of ethylbenzoylcarbinol was added dropwise with efficient stirring to an ether solution of magnesium bromide prepared from 1.5 g of Mg [5]. Five hours later, the solution was washed with hydrochloric acid, alkali solution, and then after drying with $MgSO_4$ it was distilled. 2 g of a substance boiling at 82° at 2 mm was obtained after two distillations.

0.1191 g substance: 0.3223 g CO_2; 0.0864 g H_2O. 0.1039 g substance: 0.2827 g CO_2; 0.0762 g H_2O. 0.0561 g substance: 18.6 ml 0.1 N. $Na_2S_2O_3$. Found %: C 73.86, 74.25; H 8.12 8.21; OCH_3 17.21. $C_{11}H_{14}O_2$. Calculated %: C 74.13; H 7.91; OCH_3 17.41.

II. Preparation of the Methyllactolide of Methyl-p-anisoylcarbinol.

The starting substance for the synthesis, the α-bromoethyl-p-anisyl ketone, obtained from anisole, α-bromopropionylbromide, and $AlCl_3$ had a b.p. 154-159° at 8 mm (Auwers gives a b.p. of 152-162° at 10 mm). The methyllactolide was obtained by the usual method [1,5] starting from 10 g of the bromoketone. A fraction 93-94° at 3 mm was obtained. Yield, 1.5 g.

A strong tarring occurred during the synthesis, as well as during distillation.

d_4^{20} 1.105; n_α^{20} 1.50384; MR_α 51.96. $C_{11}H_{14}O_3\digamma_3$. MR_α 51.73. 0.1226 g substance: 0.3067 g CO_2; 0.0072 g H_2O. 0.1161 g substance: 0.2894 g CO_2; 0.0722 g H_2O. 0.0496 g substance: 30.5 ml 0.1 N $Na_2S_2O_3$. Found %: C 68.16, 67.85; H 7.05, 6.93; OCH_3 31.67. $C_{11}H_{14}O_3$. Calculated %: C 68.04; H 7.22; OCH_3 31.95.

SUMMARY

1. The methyllactolides of ethylbenzoylcarbinol and methyl-p-anisoylcarbinol were newly obtained. The methyllactolide of ethylbenzoylcarbinol was comparatively stable, but it slowly polymerized upon storage. The methyllactolide of methyl-p-anisoylcarbinol polymerized very rapidly upon distillation, and upon being stored in the pure form.

2. The transformations of the methyllactolide of ethylbenzoylcarbinol were studied.

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ACYLATION OF UNSATURATED HYDRCARBONS

II. ACETYLATION OF PHENYLACETYLENE AND HEPTYNE-1 WITH ACETIC ANHYDRIDE IN THE PRESENCE OF ZINC CHLORIDE

V. N. Belov and G. Z. Shekhtman

In the first communication of the authors and Rudolfi [1], it was shown that 2-chloro-1-acetylcyclohexane was formed, in addition to tetrahydroacetophenone, during the acetylation of cyclohexene with acetic anhydride in the presence of chlorides of certain metals (zinc and stannic chlorides). It was shown that the intermediate formation of acetyl chloride or hydrogen chloride did not occur under the conditions of this reaction. On the basis of these results, which indicated that a direct transfer of the chlorine atom from the condensing medium, (metal chloride) to the ketone formed occurred, during the process of the reaction, a general scheme of this reaction was suggested.

In order to obtain supplementary experimental material on the given problem, the acetylation of certain hydrocarbons containing a triple bond, namely, phenylacetylene and heptyne-1, was effected under similar conditions (acetic anhydride in the presence of zinc chloride). In both cases only the corresponding chloroketones with an ethylenic bond could be isolated: 1-chloro-1-phenylbutene-1-one-3 (I: $R=C_6H_5$) in the case of the acetylation of phenylacetylene (yield about 31% of the theoretical), and 4-chlorononene-3-one-2 (II: $R=C_5H_{11}$) for the acetylation of heptyne-1 (yield about 20% of the theoretical). Acetylenic ketones were not detected among the reaction products. These results may be described by the following general scheme:

$$RC\equiv CH + (CH_3CO)_2O + ZnCl_2 \rightarrow RClC{=}CH{-}COCH_3 + ZnCl(OCOCH_3). \qquad (1)$$

Products were obtained in these experiments on the acetylation of acetylenic hydrocarbons with acetic anhydride in the presence of zinc chloride, which were usually formed by the reaction of acetylenic hydrocarbons with acetyl chloride in the presence of aluminum chloride. The last reaction leads, as it is known, to the formation of products of the addition of acetyl chloride to the hydrocarbon with the triple bond [2]. Chloroketone (II) was also obtained by this method, and was found to be identical with that obtained by acetylation with acetic anhydride. The only difference was in the yield of the chloroketone (in the reaction with acetyl chloride in the presence of $AlCl_3$ the yield was about 45% of the theoretical).

The results obtained in the present investigation are completely in accordance with the mechanism of the acetylation reaction of unsaturated hydrocarbons with acetic anhydride in the presence of metal chlorides suggested in the first communication on this problem [1]. It is believed that the process occurs by means of an intermediate formation of a complex consisting of all three components of the reaction mixture. Such an intermediate complex can be formed, for example, by the reaction of acetic anhydride with the molecular compound formed by the unsaturated hydrocarbon and the metal chloride, as well as by the reaction of the unsaturated hydrocarbon with the molecular compound formed by the acetic anhydride and the metal chloride. If, in the case of the acetylation of the ethylenic hydrocarbon, the intermediate complex is capable of decomposing with the formation of the saturated chloroketone, as well as the unsaturated ketone not containing a chlorine, then with acetylenic hydrocarbons, a similar complex decomposes exclusively in the direction of the formation of the chloroketone. This, however, does not exclude the possibility that the β-chloroketone may be the main product of the acetylation of ethylenic hydrocarbons, but, because of its instability, is readily transformed into the unsaturated ketone (for example, it gives a hydrogen chloride fragment to a molecule of the starting ethylenic hydrocarbon).

The considerably smaller activity of the chlorine atom in the unsaturated chloroketones (I) and (II) obtained, in comparison with that of the β-chlorovinylketones obtained from acetylene itself, must be mentioned.

As it is known, a chlorine atom in β-chlorovinylketones obtained by the addition of acyl halides to acetylene, possesses very great reactivity. This fact causes, for example, instability, and in isolated cases, because of this instability, makes the preparation of certain derivatives impossible for β-chlorovinyl ketones. Thus, according to the data of Yakubovich and Merkulova [2], β-chlorovinyl ketone semicarbazones change very easily which hinders their purification by recrystallization. The impossibility of obtaining the oxime and the hydrazone of methyl-β-chlorovinyl ketone was mentioned in the earlier communication of Cornilot and Alquier [3]. Recently, Nesmeyanov, Kochetkov, and Rybinskaya [4] showed that the reaction of alkyl-β-chlorovinyl ketones with hydrazine, as well as with arylhydrazines, leads to the formation of the 3-alkyl- and the 1-aryl-3-alkylpyrazolones which result from the participation of the chloro-as well as the carbonyl group in the reaction. This property of β-chlorovinyl ketones was used by Nesmeyanov and Kochetkov [5] for the synthesis of certain heterocyclic compounds based upon them. In particular, they, together with Semenov [6], developed a convenient method for the preparation of isoxazoles by the reaction of β-chlorovinyl ketones with hydroxylamine.

All of the above literature data are in relation to chlorovinyl ketones without substituents in the chlorovinyl radical. A considerably greater stability for the bond with the chlorine atom was found in both of the substituted β-chlorovinyl ketones (I and II) containing the amyl and phenyl group, respectively, on the carbon atom bound directly to the chlorine atom.

4-Chlorononene-3-one-2, as well as 1-chloro-1-phenylbuten-1-one-3, formed completely stable semicarbazones which did not change during many recrystallizations. A pure preparation of this chloroketone was obtained, by using the general method of decomposition (see the experimental section), from the semicarbazone of 1-chloro-1-phenylbuten -1-one-3. Both of the chloro ketones (I and II) formed other characteristic ketone derivatives retaining the chlorine atom in the molecule. Thus, oximes were obtained for ketones (I) and (II), and 2,4-dinitrophenylhydrazone for (I). These derivatives also did not shown any noticeable signs of changing upon recrystallization, or upon prolonged storage. Only the oximes of the chloroketones were formed by conducting the reaction of these chloroketones with hydroxylamine under conditions which were used by Nesmeyanov and Kochetkov for the preparation of isoxazoles; heterocyclic compounds were not found among the reaction products.

Phenylpropiolic acid was obtained by the oxidation of the chloroketone, obtained by the reaction of phenylacetylene with acetic anhydride in the presence of zinc chloride, with sodium hypochlorite. *

Therefore, the oxidation process was accompanied by the elimination of a hydrogen chloride fragment.

EXPERIMENTAL

1. Reaction of Phenylacetylene with Acetic Anhydride in the Presence of Zinc Chloride.

23 g of anhydrous zinc chloride was added gradually with stirring to a mixture of 35 g of phenylacetylene (b.p. 142 -143°, n_D^{20} 1.5472, d_4^{20} 0.9340) and 52 g of acetic anhydride. The temperature of the mixture rose from 60-80°. After the temperature dropped, the reaction mixture was heated on the water bath until complete solution of the zinc chloride, which required about 3 hours. After steam distillation of the volatile reaction products and their subsequent fractionation, (about 10.6 g of starting phenylacetylene(~30% of that used) and 13.5 g of a ketonic fraction with b.p. 132-138° (10 mm), the main part of which distilled at 132-135° (10 mm), were obtained. The chlorine content in this fraction was 16.8% (calculated for $C_{10}H_9OCl$ 19.63%); the ketone content (determined by the oximation method) based on the chloro-ketone, was 97%. The semicarbazone, obtained from this fraction, had an m.p. 180.5-181° (from alcohol).

Found: N 18.13. $C_{11}H_{12}ON_3Cl$. Calculated %: N 17.67.

A pure preparation of 1-chloro-1-phenylbuten -1-one-3 with b.p. 137-138° (10 mm) was obtained by the decomposition of the semicarbazone (heating with an aqueous oxalic acid solution with the simultaneous solution of the ketone).

n_D^{20} 1.5930; d_4^{20} 1.2373. MR_D 49.47. $C_{10}H_9OCl\,F_4$. Calculated: MR_D 49.19.

Found %: C 66.63, 66.62; H 4.90, 5.02; Cl 19.52. $C_{10}H_9OCl$. Calculated %: C 66.49; H 5.02; Cl 19.63.

The oxime, colorless needles, m.p. 93° (from alcohol).

Found %: C 61.35, 61.16; H 5.23, 5.21; N 7.26, 7.25; Cl 18.01, 18.16. $C_{10}H_{10}ONCl$. Calculated %: C 61.38; H 5.16; N 7.16- Cl 18.12.

The 2,4-dinitrophenylhydrazone, shining red crystals, m.p. 194-195° (from alcohol).

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* The oxidation was conducted in order to prove the structure of the ketone as 1-chloro-1-phenylbuten -1-one-3.

Found %: C 53.46, 53.63; H 3.80, 3.67; N 15.74, 15.46; Cl 10.13, 10.14. $C_{16}H_{13}O_4N_4Cl$. Calculated %: C 53.27; H 3.63; N 15.53; Cl 9.83.

Oxidation of 1-chloro-1-phenylbuten-1-one-3 with sodium hypochlorite. 400 ml of a sodium hypochlorite solution (containing 4.5% active chlorine) was added with continuous stirring over a 15-minute period to 8 g of the chloroketone (b.p. 133-135° at 10 mm, n_D^{20} 1.5930). The mixture was then stirred for 3 hours at 50-60°. The unreacted ketone (about 2 g) was extracted with benzene from the reaction mixture. 3.8 g of a crystalline product was obtained by the acidification of the evaporated aqueous solutions. After two recrystallizations from water, colorless, shiny needles with m.p. 138° were obtained. A mixed melting point with an authentic preparation of phenylpropiolic acid showed no depression.

Found acid number: 384. $C_9H_6O_2$. Calculated acid number: 383.2. Found %: C 73.91, 73.54; H 4.27, 4.45. $C_9H_6O_2$. Calculated %: C 73.98; H 4.14

2. Reaction of Heptyne-1 with Acetic Anhydride in the Presence of Zinc Chloride.

9 g of anhydrous zinc chloride (with efficient stirring) was added to a mixture of 20 g of heptyne-1 (m.p. 99-103°, n_D^{20} 1.4200, containing 76% of the 1-isomer)*. An increase in the temperature occurred which was decreased by water cooling. For complete solution of the zinc chloride, the reaction mixture was heated for 3 hours at 50-55° with continuous stirring. The reaction product was then poured into water and extracted with ether. The extract was washed with sodium carbonate solution and with water, and then dried with sodium sulfate After removal of the solvent and fractionation of the residue in vacuum, 5 g of the starting substance and 5.5 g of a fraction with b.p. 93-95° (10 mm) were obtained

n_D^{20} 1.4645; d_4^{20} 0.9939; found MR_D 48.54% Cl 20.10. $C_9H_{15}OCl$. Calculated: MR_D 48.17; % Cl 20.30.

Semicarbazone, colorless crystals, m.p. 137-138° (from alcohol).

Found %: N 18.11, 18.13. $C_{10}H_{18}ON_3Cl$. Calculated %: N 18.14.

A mixed melting point with the semicarbazone of the chloro-ketone obtained by the reaction of heptyne with acetyl chloride in the presence of aluminum chloride gave no depression.

An oxime was obtained by heating 1.2 g of 4-chlorononene-3-one-2 with a solution of 0.8 g of hydroxylamine hydrochloride in 10 ml of methanol for 3 hours on the water bath. The reaction mixture was diluted with 4 volumes of water, the oily layer extracted with ether. The solution was dried with sodium sulfate; after removal of the solvent, the residue was vacuum distilled. A product with b.p. 85-86° (10 mm) was obtained; n_D^{20} 1.4687.

Found %: N 7.41, 7.34; Cl 18.77, 18.69. $C_9H_{16}ONCl$. Calculated %: N 7.39; Cl 18.69.

The same oxime with b.p. 85-86° (10 mm) was obtained by conducting the reaction in the presence of sodium acetate. The nitrogen content of this oxime also corresponded to the calculated.

SUMMARY

1. It was found that chloroketones with ethylenic bonds (1-chloro-1-phenylbuten -1-one-3, and 4-chlorononene-3-one-2) were formed by the reaction of phenylacetylene and heptyne-1 with acetic anhydride in the presence of zinc chloride. Acetylenic ketones were not found among the reaction products.

2. These results prove the expressions of the mechanism of the acetylation reactions of unsaturated hydrocarbons with acetic anhydride in the presence of metal chlorides stated in the first communication.

3. The lesser reactivity of the chlorine atom in 1-chloro-1-phenylbuten -1-one-3 and 4-chlorononene-3-one 2 in comparison to that of the chlorine in β-chlorovinylketones not containing substituents on the carbon, to which the chlorine atom is directly connected, was shown.

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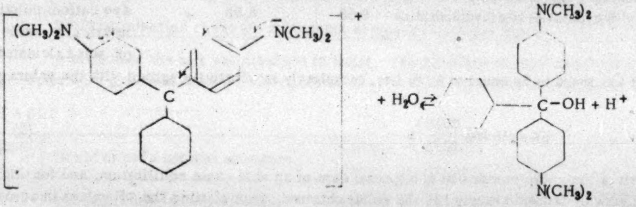
* See Consultants Bureau English translation, page 97.

DISSOCIATION OF TRIARYLCARBINOLS

O. F. Ginsburg

As early as the 90's it had been shown that basic triphenylmethane dyes were subjected to hydrolysis in aqueous solution [1]. As a result of the hydrolysis, a chemical equilibrium is gradually established in the solution, which, for example, can be represented by the following equation for malachite green:



(1)

From equation (I) it follows that the quantitative study of the hydrolysis reaction would make possible the determination of the dissociation constant of the so-called carbinol bases of the triphenylmethane dyes, which are formed by the removal of a hydroxyl group from the methane carbon atom.

The hydrobromide and hydroiodide of malachite green were obtained in chemically pure form [2], and the pH of their aqueous solutions was determined at 19± 1°. The values found are given in Table 1.

TABLE 1

Expt. No.	Name of dyes	C (moles/liter)	pH value	
			Found	Calculated for 250°
1	Malachite green hydrobromide	$1.48 \cdot 10^{-3}$	4.95	4.86
2	Malachite green iodide	$1.05 \cdot 10^{-3}$	5.02	4.94
3	Crystal violet hydrobromide	$7.45 \cdot 10^{-4}$	6.40	6.25
4	Crystal violet iodide	$9.60 \cdot 10^{-4}$	6.35	6.19

Comparatively recently, Goldacre and Phillips [2], on the basis of the experimental results obtained by a comparison of the intensities of the colors of aqueous solutions of the dyes at various pH, calculated characteristics called by them "ionization constant at equilibrium" for a whole series of basic triphenylmethane dyes, which also are hydrolysis constants of the dyes. pH values were calculated using these constants, which must correspond to those of the investigated solution.

As it is apparent from Table 1, the values found and calculated are very close, and for this reason the dissociation constants of 4,4'-tetramethyldiaminotriphenylcarbinol and 4,4',4"-hexamethyltriaminotriphenylcarbinol calculated on the basis of the pH value of the solution of the dyes and on the experimental results obtained by Goldacre and Phillips also agree satisfactorily with each other. It was found that the dissociation constants of 4,4'-tetramethyldiaminotriphenylmethylcarbinol was equal to $9.24 \cdot 10^{-8}$, and $3.76 \cdot 10^{-5}$ for 4,4',4"-hexamethyltriaminotriphenylcarbinol (at 19°).

Continuing the study of the hydrolysis of salts, from which the so-called "pseudobases" are formed by the action of alkalies, it appeared to be of interest to compare the hydrolysis constants of these salts in various solvents. For this purpose, the hydrolysis constants of 4,4'-tetramethyldiaminotriphenylcarbinol, 4,4'-tetramethyldiaminodiphenylcarbinol, diantipyrylphenylcarbinol, and 10-methyl-9-phenyl-9-hydroxy-9,10-dihydroacridine salts were determined in aqueous acetone. Hydrolysis constants were calculated from the pH values of aqueous acetone solutions containing equimolecular amounts of the carbinol and its salt. Table 2 compares the pK of the above compounds in aqueous acetone and in water.

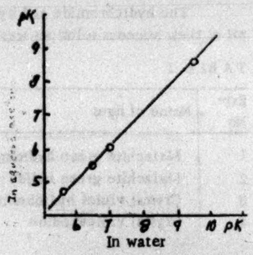
It must be mentioned that the hydrolysis constant of malachite green was calculated on the basis of experimental data obtained in the following experiment: a sample of 4,4'-tetramethyldiaminotriphenylcarbinol was dissolved in a defined quantity of aqueous acetone. When equilibrium was established in the solution obtained, the concentration of hydrogen ions was determined potentiometrically, and that of the dye cations colorimetrically, while the pK was calculated by means of formula (2), and was found to be equal to 6.06, i.e., completely satisfactorily agreed with the values given in Table 2.

TABLE 2

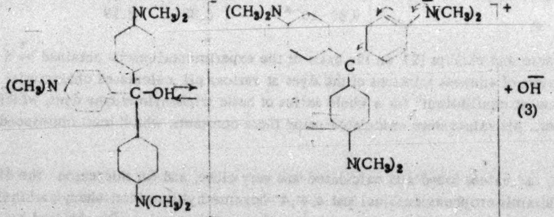
Expt. No.	Name of carbinol	pK	
		in water	in aqueous acetone
1	4,4-Tetramethyldiaminodiphenylcarbinol	5.61*	4.70
2	Diantipyrylphenylcarbinol	6.56	5.50
3	4,4'-Tetramethyldiaminotriphenylcarbinol	7.07	6.05
4	10-Methyl-9-phenyl-9-hydroxy-9,10-dihydroacridine	9.58	8.55

$$pK = pH - \log\frac{[ROH]}{[R^+]}. \qquad (2)$$

Since the hydrolysis of the above compounds is a special case of an acid-base equilibrium, and for this reason, as it was expected in view of Brensted's theory [3], the points obtained, upon plotting the pK values in aqueous acetone solution versus those in water on coordinate axes, lie with complete agreement upon a straight line, the tangent of an angle of inclination equal to 1 ee the figure).



It could be expected that, in contrast to aqueous solutions, in nitrobenzene in which solvation is impossible and which is accompanied by the transformation of the cation of the dye into a compound with a 4-covalent methane carbon atom, the dissociation of the carbinol could be very considerable. The experiments conducted confirmed these suggestions. Thus, for example, nitrobenzene solutions of 4,4'-tetramethyldiaminotriphenylcarbinol and 4,4',4"-hexamethyltriaminotriphenylcarbinol were prepared, in which the first compound was found to be dissociated to an extent of 70%, and the second, 90%.



(3)

Therefore, the results obtained in the present investigated completely confirm the suggestions of the ability of the so-called pseudo bases of Hantzsche to dissociate in various solvents with the cleavage of the hydroxyl group. This dissociation, for example, can be represented by equation (3) for 4,4',4"-hexamethyltriaminotriphenylcarbinol.

EXPERIMENTAL

1. 4,4'-Tetramethyldiaminotriphenylcarbinol

0.1001 g of 4,4'-tetramethyldiaminotriphenylcarbinol was dissolved in 70 ml of 60% aqueous acetone.

Concentration of the solution, $C = 4.13 \cdot 10^{-3}$ moles/liter, pH of the solution, 8.50, temperature, 19 ± 1°. The absorption spectrum of the solution is given in Table 3.

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* According to the results of Goldacre and Phillips [2].

TABLE 3*

λ mμ	D	λ mμ	D	λ mμ	D
500.0	0.024	600.0	0.490	630.0	0.678
520.0	0.035	620.0	0.652	635.0	0.612
540.0	0.074	622.5	0.679	640.0	0.531
560.0	0.150	625.0	0.690	650.0	0.345
580.0	0.257	627.5	0.686		

TABLE 4

λmμ	D	λmμ	D	λ mμ	D
520	0.008	600	0.212	630	0.365
540	0.027	610	0.295	640	0.285
560	0.070	620	0.366	650	0.178
580	0.131	625	0.375		

The solution obtained was acidified with a 0.1 N hydrochloric acid solution and diluted 500 times with 60% aqueous acetone. On the following day, the absorption spectrum of the dye solution obtained was taken, whose pH was 4.50 (temperature 19 ±1°). The concentration of the dye in the solution was C 0.82 · 10^{-5} moles/liter.

The absorption spectrum of the solution obtained is given in Table 4.

2. Determination of the pH of Aqueous Solutions of Several Dyes

A sample of the salt was dissolved in water. The pH of the solution was measured in all experiments on a pH meter with glass and calomel electrodes at 19 ±1°. The results obtained are given in Table 5.

TABLE 5

Expt. No.	Name of the dissolved substance	Sample (in g)	Amount of water (ml)	pH
1	Malachite green hydrobromide	0.0607	100	4.95
2	Malachite green hydroiodide	0.0481	100	5.02
3	Crystal violet hydrobromide	0.0505	150	6.40
4	Crystal violet hydroiodide	0.0479	100	6.35
5	Antipyrine orange nitrate	0.0797	100	4.70
6	10-Methyl-9-phenylacridinium iodide	0.0900	100	6.10
		0.0912	100	6.10

3. Determination of the pH of Several Salts in Aqueous Acetone

A sample of the substance was dissolved in 70 ml of 60% aqueous acetone. If the salt was used, 0.5 equivalents of sodium hydroxide was added; if the bases were used, 0.5 equivalents of hydrochloric acid. On the following day, the pH of the solution was determined at 19 ± 1. The results obtained are given in Table 6.

TABLE 6

Expt. No.	Name of the dissolved substance	Sample	Addend of 0.1 N sol. (ml)		pH
			HCl	NaOH	
1	Malachite green hydroiodide	0.0588	–	0.72	6.05
2	4,4'-Tetramethyldiaminotriphenylcarbinol	0.1886	2.72	–	6.05
3	Antipyrine orange nitrate	0.1004	–	0.95	5.50
4	Diantipyrylphenylcarbinol	0.1231	1.28	–	5.50
5	4,4'-Tetramethyldiaminodiphenylcarbinol	0.1102	2.04	–	4.70
6	10-Methyl-9-phenylacridinium iodide	0.1448	–	1.82	8.60
		0.1515	2.64	–	8.60
7	10-Methyl-9-phenyl-9-hydroxy-9,10-dihydroacridine	0.1517	2.64	–	8.50
		0.1523	2.65	–	8.55

4. Absorption Spectra of Solutions of the Dyes and their Carbinol Bases in Nitrobenzene

a) 4,4'-Tetramethyldiaminotriphenylcarbinol and malachite green hydroiodide were dissolved in nitrobenzene. The solutions obtained were heated for 2 hours on the water bath at 80°, cooled, and the absorption spectra taken on the following day (Table 7).

The applicability of Beer's law to solutions of malachite green in nitrobenzene was shown previously [4].

The concentration of the dye cation in the nitrobenzene solution of 4,4'-tetramethyldiaminotriphenylcarbinol was equal to 4.0 · 10^{-5} g-ions/liter.

b) Solutions of 4,4',4"-hexamethyltriaminotriphenylcarbinol and crystal violet hydroiodide in nitrobenzene were prepared. The absorption spectra were taken 3 days later (Table 8).

The concentration of the dye cation in the nitrobenzene solution of 4,4',4"-hexamethyltriaminotriphenylcarbinol was equal to $7.2 \cdot 10^{-5}$ g-ions/liter.

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* All of the spectrophotometric measurements were effected on the SF-11 spectrophotometer.

TABLE 7

λ mμ	D	
	Malachite green hydroiodide $C = 4.3 \cdot 10^{-5}$ moles/liter	4,4'-Tetramethyldiaminotriphenylcarbinol $C = 5.8 \cdot 10^{-5}$ moles/liter
600	0.42	0.40
620	0.85	0.81
630	1.09	1.04
635	1.15	1.09
640	1.06	1.01
650	0.79	0.75

TABLE 8

λ mμ	D	
	Crystal violet hydroiodide $C = 5 \cdot 10^{-5}$ moles/liter	4,4',4"-Hexamethyltriaminotriphenylcarbinol $C = 8 \cdot 10^{-5}$ moles/liter
550	0.237	0.444
590	0.450	0.670
600	0.497	0.720
605	0.468	0.700
610	0.468	0.658
620	0.381	0.502

SUMMARY

The carbinol compounds of the triarylmethane dyes (the so-called "pseudo bases" of Hantzsch) are capable of dissociation with the cleavage of the hydroxyl group and the formation of dye cations. This dissociation occurs in other solvents, as well as in water.

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CYCLOALKYLATION OF AROMATIC COMPOUNDS

VII. CONDENSATION OF CYCLOHEXANOL WITH CHLOROBENZENE

N. G. Sidorova and I. S. Lapovok

In the previous investigations [1], it was shown that the alkylation of aromatic hydrocarbons with cyclic alcohols in the presence of aluminum chloride gave good yields of monoalkylated products. It seemed of interest to try this method upon the halobenzenes, and in particular, upon chlorobenzene. For this reason, the study of the condensation of chlorobenzene with cyclohexanol in the presence of aluminum chloride was conducted. In order to compare the various methods of alkylation, the alkylation of chlorobenzene with cyclohexene in the presence of aluminum chloride and with cyclohexanol in the presence of phosphoric acid was also studied.

The cycloalkylation of the halobenzenes has been studied many times in the past. Their condensation with cyclohexanol in the presence of $AlCl_3$ [2], H_2SO_4 [3], and BF_3 [4] has been reported. The maximum yields (34-50% of theory) were obtained by the alkylation of chlorobenzene, the lowest, with the alkylation of iodobenzene. In both cases, only the obtaining of the p-isomers is reported.

The condensation of halobenzenes with cyclohexene was effected in the presence of $AlCl_3$ [5, 6] and H_2SO_4 [7]. The systematic study of the reaction in the presence of sulfuric acid conducted by Truffault is of the greatest interest. However, even under optimum conditions the yield of the p-cyclohexylbenzene by means of this reaction did not exceed 44% of theory. Similar yields were obtained with the condensation under the influence of aluminum chloride. Considerably better results (72% of p-cyclohexylchlorobenzene and 65% of p-cyclohexylbromobenzene) were obtained by the use of chlorocyclohexane and $AlCl_3$ [8]. An analogous condensation of bromobenzene with chlorocyclohexane was also effected [9]. This investigation is of interest because the authors investigated the reaction products in detail and showed that they consisted of all three isomers of cyclohexylbromobenzene, whereas all of the other investigators reported only the obtaining of p-cyclohexylhalobenzenes. It is interesting that the formation of o- and m-isomers, in addition to the p-isomers, has been frequently observed during the alkylation of halobenzenes with aliphatic compounds [10].

The alkylation of chlorobenzene with cyclohexanol in the presence of aluminum chloride was studied in greater detail. The aim of this investigation was not only to find those conditions which would lead to good yields of alkylation products, but also the effect of the conditions upon the formation of the different isomers. 0.9-1.0 moles $AlCl_3$ per mole of cyclohexanol was necessary for the obtaining of good yields A favorable effect was shown by an excess of chlorobenzene and by a decrease in temperature. The temperature affects not not only the yields of the alkylation products, but also their compositions: the product obtained at high temperatures consisted wholly of p-cyclohexylchlorobenzene, while that obtained by condensation at 0°, contained considerable amounts of the o-isomer. The order of the addition of the reactants was of great effect. Better results were obtained when the $AlCl_3$ was added gradually to a mixture of chlorobenzene and cyclohexanol. Considerable amounts of higher boiling products and tars were obtained when cyclohexanol was added to a mixture of chlorobenzene and aluminum chloride, in addition to cyclohexylchlorobenzene. This is explained by the fact that, with the gradual addition of the alcohol, the first portions of it come in contact with a large amount of aluminum chloride, whose excess usually leads to accumulation of poly-substituted products. Under optimum conditions, as high as 85% yields of cyclohexylchlorobenzene were attained.

The identification of the reaction products was effected by oxidizing them to the chlorobenzoic acids. In one case, the method of dehydrogenation with bromine, usually used for cyclic hydrocarbons [11], was applied. Its use for the dehydrogenation of cyclohexylchlorobenzene gave good results.

The product obtained by condensation at 95° was the pure p-isomer, since only p-chlorobenzoic acid was obtained upon oxidation with nitric acid. The condensation product at 0° consisted of approximately 2/3rds of the p- and 1/3rd of cyclohexylchlorobenzene, which was shown by its oxidation to the corresponding chlorobenzoic acids. The product obtained at 20° was a mixture of o- and p- isomers with the latter predominating. The m- isomer could not be detected in any case.

The following were varied during the condensation of chlorobenzene with cyclohexene in the presence of aluminum chloride: the amount of catalyst and chlorobenzene, the order of addition of the reagents, and the reaction time. However, the change of the conditions had little effect upon the results in this case. The product was obtained in low yield (17-26% of the theoretical amount) and always contaminated with the dimer of cyclohexene.

The condensation of cyclohexanol with chlorobenzene in the presence of phosphoric acid could not be accomplished even though analogous reactions with aliphatic alcohols have been reported [12]. In all cases, only the dimer and polymers of cyclohexene were obtained. These results are explained by the easy dehydration of cyclohexanol and the ability of cyclohexene to polymerize readily.

EXPERIMENTAL

Condensation of Chlorobenzene with Cyclohexanol in the Presence of Aluminum Chloride

The reaction was conducted in the usual apparatus with a mechanical stirrer. The results of the condensations giving the maximum yields are reported below.

13.3 g (0.1 mole) of aluminum chloride was added in small portions over a 1-hour period with efficient stirring to a mixture of 100 ml (1 mole) of chlorobenzene and 10 g (0.1 mole) of cyclohexanol. If the addition of $AlCl_3$ was made at 20°, a violent evolution of hydrogen chloride started after the addition of all of the catalyst, which continued for 15-20 minutes; the mixture warmed up slightly with this. The mixture was allowed to stand until the following day in order to complete the reaction, and then decomposed in the usual manner. In the case of the reaction at 0°, the mixture thickened after the addition of part of the aluminum chloride, and required the addition of 100 ml more of chlorobenzene. A slow evolution of hydrogen chloride started after the addition of all of the $AlCl_3$, and continued for 2 days. During this time the mixture was kept at 0-5°. After the decomposition of the reaction mixture, the chlorobenzene layer was washed, dried, and distilled. In both cases the yield of cyclohexylchlorobenzene with b.p. 120-121° (7 mm) was identical, 16.6 g (85% of the theoretical amount). Repeat condensations with three-fold quantities of the reagents gave the same results. Increasing the reaction temperature to 50-95°, lowered the yield to 65-70%.

Cyclohexylchlorobenzene obtained at 95° had the following constants:

B.p. 121° (7 mm); d_4^{20} 1.0637; n_D^{20} 1.5384; MR_D 57.23. $C_{12}H_{15}Cl$; calculated MR_D 56.67.

p-Chlorobenzoic acid with m.p. 230° was obtained by oxidation with nitric acid (d 1.111) in a sealed tube at 130-150° for 10 hours. After one recrystallization from water, the melting point rose to 238° (uncorr.). p-Chlorobenzoic acid melts at 242° according to the literature.

Cyclohexylchlorobenzene obtained at 20° had the following constants:

B.p. 121° (7 mm); d_4^{20} 1.0688; n_D^{20} 1.5403; MR_D 57.12; calculated MR_D 56.67. Found %: Cl 18.37. $C_{12}H_{15}Cl$. Calculated %: Cl 18.25.

Oxidation with nitric acid gave a product melting at 156-180°. Fractional crystallization gave p-chlorobenzoic acid, m.p. 238°, and crystals, melting at 140-160°, from which no individual substance could be isolated.

Dehydrogenation. The calculated amount of bromine was added dropwise to cyclohexylchlorobenzene heated to 160° in a three-neck flask with a thermometer, dropping funnel, and a reflux condenser. After the addition of all of the bromine, the heating was continued for several hours, the mixture allowed to stand until the evolution of hydrogen bromide stopped, and distilled. The following fractions were obtained: I, b.p. 267-270°; II, 274-276°; III, 280-283°. p-Chlorodiphenyl with m.p. 74° (from ligroin) was isolated from the second and third fraction upon cooling. The liquid fraction distilled at 267-270°. It corresponded to o-chlorodiphenyl according to boiling point.

Nitration [8] of cyclohexylchlorobenzene gave an oil which partially crystallized. Pure 4-chloro-2,6-dinitrocyclohexylbenzene with m.p. 92° was obtained upon recrystallization from alcohol.

Cyclohexylchlorobenzene obtained at 0° had the following constants:

B.p. 120° (7 mm); d_4^{20} 1.0691; n_D^{20} 1.5402; MR_D 57.10. $C_{12}H_{15}Cl$; calculated MR_D 56.67.

Oxidation with dilute nitric acid gave a mixture of o- and p-chlorobenzoic acids, which were separated by extraction with hot water and fractional crystallization with water; p-chlorobenzoic acid with m.p. 238° composed approximately 2/3 of the total amount of the acids, while o-chlorobenzoic acid with m.p. 142°, about 1/3.

Condensation of Chlorobenzene with Cyclohexene in the Presence of Aluminum Chloride

The reaction was conducted with mechanical stirring. The order of addition of the reagents was always the same, cyclohexene was added to a mixture of chlorobenzene and $AlCl_3$. The amount of $AlCl_3$ was varied from 0.4 to 1.0 mole per mole of cyclohexene; the chlorobenzene was always taken in ten-fold excess. The reaction temperature was varied from 20-40°. The yield of the fraction with b.p. 120-125° (7 mm) was 17-26% of the theoretical amount. In addition, considerable amounts of high boiling fractions was obtained. All of the products decolorized a solution of potassium permanganate and bromine water.

Condensation of Chlorobenzene with Cyclohexanol in the Presence of Phosphoric Acid

The reaction was conducted in a three-necked flask with a reflux condenser and mechanical stirrer. The phosphoric acid (d 1.86) was prepared by evaporating commercial acid in a platinum dish. The reaction was conducted under various conditions. The amount of chlorobenzene was varied from 5 to 10 moles, and the amount of phosphoric acid from 2 to 10 moles per mole of cyclohexanol.The temperature was varied from 55 to 120°, and the heating time from 1 to 10 hours. In spite of all of the variations in conditions, the reaction either did not occur, or cyclohexene with b.p. 79-82°, its dimer with b.p. 60-63° (4 mm), and polymers with b.p. 63-150° (4 mm) were obtained as reaction products. The reaction products gave a positive reaction for a double bond and a negative one for halogen.

SUMMARY

1. The condensation of chlorobenzene with cyclohexanol was studied and conditions which gave yields of cyclohexylchlorobenzene of up to 85% of theory were found.

2. It was shown that p-cyclohexylchlorobenzene was formed upon conducting the condensation with heating, whereas at 0-20°, a mixture of o- and p-cyclohexylchlorobenzene was obtained, with the latter predominating.

3. The condensation of chlorobenzene with cyclohexanol in the presence of phosphoric acid could not be accomplished. The phosphoric acid behaved as a dehydrating and polymerizing agent.

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* See Consultants Bureau English Translation, page 1015.

[illegible] with the water and reaction [illegible] approximately [illegible] of the total amount of the [illegible]

Condensation of [illegible]
[illegible]

The reaction was conducted with [illegible] and mixing. The order of addition of the [illegible] was added to a mixture of [illegible] The amount of [illegible] was varied from [illegible] to [illegible] mole per mole of cyclohexanone, [illegible] The reaction temperature was varied from [illegible] The yield of the reaction [illegible] amount. In addition considerable amounts of [illegible] we obtained a fraction of [illegible]

Condensation of [illegible] in the Presence of Phosphoric Acid

The reaction was conducted in a three-necked flask with a reflux condenser and [illegible] stirrer. Phosphoric acid [illegible] The reaction was [illegible] conditions. The amount of [illegible] was varied from [illegible] to 10 moles per mole of cyclohexanone, the temperature was varied from [illegible] and the heating time from 1 to 10 hours. In spite of all the variations in conditions, the [illegible] with b.p. [illegible] and [illegible] The reaction [illegible]

SUMMARY

1. The condensation of [illegible] of 20 to 30% of theory were found.

2. It was shown that [illegible]

3. The condensation of [illegible] The phosphoric acid behaves as a [illegible]

[1] [illegible]

[2] [illegible]

[3] [illegible]

[4] [illegible]

[5] [illegible] Patent [illegible] Chem. Abs. [illegible]

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Received December [illegible]

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TRANSETHERIFICATION OF DIALKYLAMINOMETHYLALKYL ETHERS

K. G. Mizuch and R. A. Lapina

Dialkylaminomethylalkyl ethers of the general formula $\begin{matrix}R\\R\end{matrix}\!\!>NCH_2OR$ (I) are characterized by increased reactivity, and are separated in this way from simple ethers. This is especially graphically illustrated by the reaction of (I) with organo-magnesium compounds [1].

The increased reactivity of (I) can be explained by the tendency of the C—O in these compounds to polarize as a result of which a center of electrophyllic activity arises at the carbon atom of the methylene group, which facilitates neucleophyllic substitution.

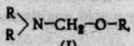
The formation of $(C_2H_5)_2NCH_2Cl \cdot 6H_2O$, isolated by Stewart and Bredley [2] by the neutralization of N-diethylaminomethylisobutyl ether with hydrochloric acid, and the formation of various dialkylaminomethyl derivatives with the participation of (I), reported by a series of authors [3-5], can be assigned to this type of reaction.

MacLeod and Robinson [3] obtained, by the action of diethylaminomethylethyl ether upon acetophenone and 2,4-dinitrotoluene, β-diethylaminopropiophenone and 2,4-dinitro-β-diethylaminoethylbenzene, respectively, which they characterized as the chloroplatinates. Heou-Feo-Tseou and Chang-Tsing-Yang [4] obtained the piperidinomethyl derivatives by the action of piperidinomethylethyl ether on naphthol, naphthylamines, cresols, and several other substituted phenols. Burckhalter and co-workers [5] used (I) for the preparation of dialkylaminomethylphenols.

The ease with which these reactions proceeded led to the suggestion that (I) is capable of reacting with other nucleophyllic reagents.

The presence of the group $>N{-}CH_2O{-}$ in (I) makes it possible to regard them not only as ethers, but also as the nitrogen analogs of formals, monoaminoformals Such a view has been given more than once for compounds similar in structure. The structural analogy between acetals and bis-(dialkylamino)methylenes, on one hand [6], and acetals and bis-(stearylamido)methylene, on the other [7] has been pointed out.

Upon comparing (I) with formulas (II) and bis-(dialkylamino)methylenes (III), an undoubted similarity in their structures is apparent.

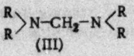


$$\begin{matrix}R\\R\end{matrix}\!\!>N{-}CH_2{-}O{-}R,$$

(I)

$$R{-}O{-}CH_2{-}O{-}R,$$

(II)



$$\begin{matrix}R\\R\end{matrix}\!\!>N{-}CH_2{-}N\!\!<\!\!\begin{matrix}R\\R\end{matrix}$$

(III)

This resemblance is not limited to the formal formula alone. It is known that (I), as well as (II) are readily hydrolyzed in aqueous solutions by the action of acids and possess stability to alkalies. However, other reactions reported for formals were not applied to dialkylaminomethylalkyl ethers.

One of these reactions which has been more thoroughly studied for formals is the alcoholysis reaction, which can be regarded as a neucleophyllic substitution at the carbon atom of the methylene group.

Delépine [8] obtained diamylformal as one of the reaction products by heating methylal with amyl alcohol in the presence of catalytic amounts of hydrochloric acid Mikhitoryan [9] found that the lighter alkoxyl groups were displaced from the acetals during the reaction of methylacetal or butyraldehyde acetal with pentaerythritol in the presence of p-toluenesulfonic acid.

Kursanov, Setkina, and Rodionov [10] report on the possibility of alkoxyl radicals of formals to be exchanged by heavier ones on heating them with alcohols in the absence of catalysts.

Based upon the structural analogy of formals to dialkylamino methylalkyl ethers and the ability of these and others to substitute neucleophyllically, it was suggested that the alcohols reaction would proceed with dialkylamino methylalkyl ethers.

This suggestion was confirmed experimentally [11]. Upon heating diethylaminomethylethyl ether (IV) with hexyl alcohol at 130-135° under conditions of simultaneous removal of the ethyl alcohol formed, diethylaminomethylhexylether (V) was obtained in a 76% yield:

$$\underset{(IV)}{(C_2H_5)_2NCH_2-OC_2H_5} + C_6H_{13}OH \rightarrow \underset{(V)}{(C_2H_5)_2NCH_2-OC_6H_{13}} + C_2H_5OH.$$

This same alcoholysis reaction with high yields (up to 80%) proceeded with other primary alcohols of various structure: n-butyl, isobutyl, n-decyl, benzyl, cinnamyl, as well as with butylglycol and phenylglycol. In addition to primary alcohols, the alcoholysis reaction was effected with secondary alcohols: isobutyl alcohol and cyclohexanol.

As it was expected experiments conducted with tertiary alcohols methylethylisoamylcarbinol and triphenylcarbinol, did not lead to the formation of dialkylaminomethylalkyl ethers containing a tertiary alcohol residue, which agrees with the unusual characteristics of the hydroxyl found at the tertiary carbon atom [12]. Upon effecting this reaction under conditions reported in experiments with primary and secondary alcohols, the decomposition of (IV) occurred with the formation of ethyl alcohol, and a large part of the starting tertiary alcohol was recovered. The alcoholysis was also effected with diisobutylaminomethyl ethyl (VI) by the reaction of the latter with n-decyl alcohol.

A large part of the ethers prepared by this method were newly synthesized by the authors. Several of these were identified by means of ethers obtained by the reaction of dialkylamine, paraformaldehyde, and the corresponding alcohol.

Another interesting reaction is the ability of mixed formal to become symmetrical (exchange of alkoxyl groups) under the influence of catalyst or with increased temperatures

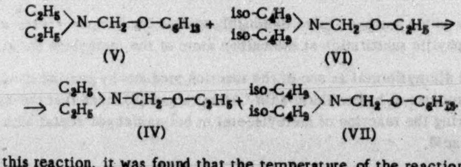
Shostakovsky and Gershtein [13] observed the formation of symmetrical acetals during the distillation of mixed ones.

Kursanov, Setkina, and Rodionov [10] obtained two symmetrical acetals in addition to the asymmetrical ones by the reaction of quaternary ammonium salts with various alcohols, which formed as a result of symmetrization of the initially formed asymmetrical acetals.

Prilezhaeva, Shapiro, and Shostakovsky [14] showed the ability of α,β-dialkoxydiethylsulfides, having the structure of monoacetals $(CH_3-CH\left\langle{}^{SCH_2CH_2OR}_{OR}\right.)$, to disproportionate with the formation of equimolecular amounts of dialkylacetals and dialkoxydiethylmercaptals.

It also could have been supposed that dialkylaminomethylalkyl ethers (I) would possess the ability of interchanging alkoxy groups. It was considered that experimental proof of transetherification would be obtained by choosing (I) so that one of the two newly formed ethers would have considerably lower boiling point than the other, and could for this reason be removed from the sphere of the reaction. This property would enable a maximum shift of the reaction in the desired direction.

Thus, for example, the following two new ethers, must be formed by the interaction of diethylaminomethylhexyl ether (V) with diisobutylaminomethylethyl ether (VI): diethylaminomethylethyl (IV) with b.p. 132°, and the considerably higher boiling diisobutylaminomethylhexyl ether (VII):



$$\underset{(V)}{{}^{C_2H_5}_{C_2H_5}\!>\!N-CH_2-O-C_6H_{13}} + \underset{(VI)}{{}^{iso\text{-}C_4H_9}_{iso\text{-}C_4H_9}\!>\!N-CH_2-O-C_2H_5} \rightarrow$$

$$\rightarrow \underset{(IV)}{{}^{C_2H_5}_{C_2H_5}\!>\!N-CH_2-O-C_2H_5} + \underset{(VII)}{{}^{iso\text{-}C_4H_9}_{iso\text{-}C_4H_9}\!>\!N-CH_2-O-C_6H_{13}}$$

Upon effecting this reaction, it was found that the temperature of the reaction had to be raised to 170-180° in order to distill the readily distilling transetherification product (which considerably exceeded the temperature of the mixture during the alcoholysis reaction). In addition, the temperature of the distilling liquid was much lower than the boiling point of the expected ether (IV). An investigation of the lower-boiling distillate obtained showed that ethyl alcohol was the main component part; only very small amounts of ether (IV) were contained in it. The second expected ether was isolated with a yield of 52.4% upon vacuum distillation of the reaction mixture.

Analogous results were obtained upon the transetherification of other dialkylaminomethylalkyl ethers. Methyl or ethyl alcohol was the main component of the lower boiling distillate upon the interaction of diisobutylaminomethylethyl ether (VI) and diethylaminomethylbutylglycol ether, diethylaminomethyl-n-decyl ether and hexamethyleneiminomethylmethyl ether, as well as diethylaminomethylphenylglycol ether and hexamethyleneiminomethylmethyl ether.

The expected low boiling diethylmethylmethyl ether (b.p. 115°) and (IV) (b.p. 132°) were found in very small amounts. On the other hand, the higher boiling ethers, hexamethyleneiminomethylphenylglycol, hexamethyleneiminomethyldecyl, and diisobutylaminomethylbutylglycol ethers were isolated in yields of 80.7, 61.4 and 46% respectively. The presence of methyl and ethyl alcohol in the reaction products was unexpected and indicated the possible decomposition of diethylaminomethylethyl and diethylaminomethylmethyl ethers at the temperature conditions chosen for the reaction.

For this reason, the thermal stability of (IV) was investigated at the temperatures corresponding to those in the reaction.

Onheating (IV) in a sealed tube to 184° (in aniline vapors) for 12 hours, a dark tarry liquid was obtained which differed in outer appearance from the starting ether. Ethyl alcohol and bis(diethylamino)methylene were identified in the reaction products by means of fractional distillation. (IV) was not isolated.

In an analogous manner it was shown that diethylaminomethylhexyl ether (V) was subjected to decomposition to a certain degree by heating for 3 hours at 170 - 180° with the formation of diethylamine, hexyl alcohol, and nitrogen-containing substances.

At the present time, no sort of scheme can be suggested for the thermal decomposition of dialkylaminomethyl alkyl ethers which lead to the formation of alcohols (compare [13]).

These experiments placed in doubt the results obtained on the transetherification of the ethers (I) since the formation of diisobutylaminomethylhexyl, hexamethyleneiminomethylphenylglycol, heaxamethyleneiminomethyldecyl, and diisobutylaminomethylbutylglycol ethers could have occurred as a result of a series of other transformations caused by the different thermal stabilities of ether containing lighter and heavier alkoxyl residues.

In order to prove more exactly the course of the transetherification reaction of the ethers (I), experiments were conducted in order to determine the temperature conditions at which the thermal decomposition of (IV) did not occur, or occurred to the minimum degree.

It was found that only 1% of ethyl alcohol was formed after heating (IV) for 75 hours in a sealed tube at 132° (in vapors of chlorobenzene). The remaining product was, judging by the nitrogen content and refraction, unchanged (IV). After determination of the relative stability of (IV) at 132°, the transetherification experiment of (V) and (VI) was repeated under these conditions: the investigation of the reaction products was effected by vacuum distillation at temperatures also not greater than 132° in the reaction. Ethyl alcohol was not detected in this experiment. As a result of the reaction (IV) was obtained with a yield of 28.6% and (VII) with a yield of 22.7% of the theoretical.

Therefore, it was shown that alkoxyl group interchange reaction between various dialkylaminomethylalkyl ethers truly occurred.

EXPERIMENTAL

The alcoholysis of the dialkylaminomethylalkyl ethers was conducted in a four-necked flask with a mechanical stirrer, dropping funnel, out-going condenser, and thermometers which showed the temperature of the reaction mixture and the distilling vapors. A mixture of the alcohol and some dialkylaminomethylalkyl ether was placed into the flask, and the heating of the reaction mixture was begun. The indication of the start of the reaction was the formation of a distillate of ethyl (or methyl)alcohol. The starting temperature of the alcoholysis reaction differed in relation to the starting substances used. In order to avoid side processes, the rest of (I) was gradually added at this temperature After the addition of (I), the temperature of the reaction mixture was raised to 140 - 150°* and was kept at this temperature until the distillation of the lower-boiling alcohol stopped completely.

The alcoholysis of diethylaminomethylethyl ether with n-hexyl alcohol is given below as a typical experimental report.

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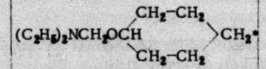
* The alcoholysis of diisobutylaminomethylethyl ether with decyl alcohol occurred at a higher temperature.

Alcoholysis of Dialkylaminomethylalkyl Ethers (I)

Expt. No.	Starting alcohol	Dialkylaminomethylalkyl ether					MR_D	
		Structure of ether obtained	Yield (%)	Boiling point (°C)	d_4^{20}	n_D^{20}	found	calculated
1	N-Butyl alcohol	$(C_2H_5)_2NCH_2OC_4H_9$	69.59	172 - 174				
2	Isobutyl alcohol	$(C_2H_5)_2NCH_2OC_4H_9$-iso	72.5	163 - 165				
3	N-Decyl alcohol	$(C_2H_5)_2NCH_2OC_{10}H_{21}$*	32.51	146 - 147 at 12 mm				
4	Benzyl alcohol	$(C_2H_5)_2NCH_2OCH_2C_6H_5$*	66.1	122 - 124 at 15 mm	0.9359	1.4938	60.10	59.75
5	Butylglycol	$(C_2H_5)_2NCH_2OCH_2CH_2OC_4H_9$*	71.91	111 at 13 mm	0.8641	1.4271	60.42	60.38
6	Phenylglycol	$(C_2H_5)_2NCH_2OCH_2CH_2OC_6H_5$*	61.65	142 - 146 at 10 mm	0.9991	1.4969	65.39	66.01
7	Cinnamyl alcohol	$(C_2H_5)_2NCH_2OCH_2CH:CHC_6H_5$*	78.61	149 - 152 at 9 mm	0.9562	1.5260	70.40	68.52
8	Cyclohexanol		70.15	93 - 94 at 10 mm	0.8839	1.4493	56.26	56.54
9	Isooctyl alcohol	$(C_2H_5)_2NCH_2OC_8H_{17}$-iso	84.01	111 at 10 mm	0.8230	1.4293	67.51	67.97
10	N-Decyl alcohol	iso-$(C_4H_9)_2NCH_2OC_{10}H_{21}$*	72.41	160 - 161 at 7 mm	0.8238	1.4330	94.50	95.68

Notes. Literature data for ether of experiment 1: b.p. 172 – 173° at 756 mm; for ether experiment 2: b.p. 165° at 760 mm. Ethers of experiments 7 and 9 were also obtained by the reaction of diethylamine, paraformaldehyde, and the corresponding alcohol; b.p. 152 at 10 mm, and 111 – 112 at 10 mm; n_D^{20} 1.5260 and 1.4292, respectively.

Diethylaminomethyl-N-hexyl Ether (V)

a) 51 g of n-hexyl alcohol (b.p. 157 – 158°), 15 g of freshly distilled diethylaminomethylethyl ether (IV) (b.p. 132 – 134°) were placed into a flask, and the mixture was heated until the appearance of an ethyl alcohol distillate (130°). 57 g more of (IV) was added at this temperature at such a rate that the temperature of the distilling vapors did not exceed 78 – 80° (in order to avoid the distillation of (IV) with the vapors of the ethyl alcohol). At the end of the addition of (IV), the mixture was heated within 30 minutes up to 145° and kept at this temperature until the distillation of ethyl alcohol stopped (about 2 hours). 16.2 g of a distillate was obtained which consisted of ethyl alcohol with a small contamination of a nitrogen-containing compound (nitrogen content 0.9%). (V) was isolated after fractional distillation of the reaction mixture (71 g; yield 76%).

B.p. 90 – 91° at 10 mm; d_D^{20} 0.8201; n_D^{20} 1.4260; MR_D 58.53; calculated 58.74.

3.428, 3.740 mg substance: 8.822, 9.656 mg CO_2; 4.110, 4.424 mg H_2O. 0.2415, 0.2346 g substance: 13.0, 12.84 ml 0.1N HCl. Found %: C 70.23, 70.46; H 13.41, 13.24; N 7.54, 7.67. $C_{11}H_{25}ON$. Calculated %: C 70.53; H 13.45; N 7.48.

The diethylaminomethyl-n-hexyl ether (V) obtained by the reaction of diethylamine, paraformaldehyde, and n-hexyl alcohol, had the following constants: b.p. 91 – 92° at 10 mm; d_4^{20} 0.8205; n_D^{20} 1.4259.

b) 20.5 g of diethylaminomethylmethyl ether (b.p. 114 – 115°) was added to a mixture of 20.4 g of n-hexylalcohol and 5.2 g of the former at 130 – 135° over a period of 1 hour. The reaction mixture was then heated for 1 hour and 30 minutes at 140° until the distillation of methyl alcohol stopped. The temperature of the distilling vapors was 65 – 66° (weight of the distillate 5.75 g; nitrogen content 1.55%). Diethylaminomethyl-n-hexyl ether (28.35 g; yield, 75.8%) with b.p. 92° at 10 mm was isolated by fractional distillation of the reaction mixture.

* Ethers designated by a star are new compounds.

Alcoholysis of Dialkylaminomethylalkyl Ethers (I) – (continued)

Dialkylaminomethylalkyl ether					
Elementary analysis					
Found			Calculated		
C	H	N	C	H	N
67.67, 67.92	13.15, 12.91	8.73, 8.73	67.87	13.29	8.79
67.54, 67.68	13.21, 13.01	8.91, 8.98	67.87	13.29	8.79
		5.51, 5.48			5.75
74.26, 74.09	10.00, 9.87	7.06, 7.04	74.56	9.91	7.23
64.71, 64.91	12.04, 12.27	7.15, 7.12	64.98	12.39	6.89
70.29, 70.36	9.15, 9.36	6.30, 6.24	69.91	9.48	6.27
77.08, 77.00	9.32, 9.63	6.32, 6.33	76.68	9.66	6.39
71.31, 71.35	12.54, 12.38	7.57, 7.56	71.29	12.51	7.56
72.40, 72.27	13.46, 13.63	6.42, 6.47	72.49	13.57	6.50
76.30, 76.13	13.54, 13.45	4.50, 4.48	76.18	13.80	4.68

The experiments on the alcoholysis reaction of diethylaminomethylethyl ether with alcohols of various structure (experiments 1 – 9) are given in the table; experiment 10 was conducted with diisobutylaminomethyl ether.

Transetherification of Diethylaminomethyl-n-hexyl Ether (V) and Diisobutylaminomethyl Ethyl Ether (VI)

a) Transetherification at 175 – 200°. A mixture consisting of 33.3 g of (V) and 10 g of (VI) was heated until the appearance of a distillate (170 – 174°), and 26.7 g more of (VI) was added at this temperature over a one hour period. At the end of the addition of (VI), the temperature of the reaction mixture was raised to 200° and kept there for 1 hour until the distillation stopped. The temperature of the distilling vapors was 64 – 78°. The following were isolated upon the redistillation of the distillate obtained (15.3 g) through a laboratory rectification column: 1) ethyl alcohol (7.1 g), b.p. 77 – 78°; it was identified as the nitrobenzoate with m.p. 56 – 56 5° from methyl alcohol; 2) diethylaminomethylethyl ether (IV) (3.7 g).

B.p. 132 – 134°; d_4^{20} 0.8090; n_D^{20} 1.4110; MR_D 40.24; calculated 40.26.

0.1852, 0.1739 g substance: 14.05, 13.29 ml 0.1N HCl. Found %: N 10.63, 10.71. $C_7H_{17}ON$. Calculated %: N 10.68.

The reaction mixture was a dark-colored, lively liquid in external appearance, from which diisobutylaminomethylhexyl ether (VII) (22.7 g; yield, 52.46%) was obtained upon two fractional vacuum distillations.

B.p. 132.4 – 133.6° at 12 mm; d_4^{20} 0.8188; n_D^{20} 1.4363; MR_D 77.77; calculated 77.21

3.363, 3.526 mg substance: 9.150, 9.580 mg CO_2; 3.984, 4.240 mg H_2O. 0.3066, 0.3197 g substance: 13.22, 14.02 ml 0.1N HCl. Found %: C 74.24, 74.16; H 13.27 13.46 N 6.04, 6.14. $C_{15}H_{33}ON$. Calculated %: C 74.01; H 13.66 N 5.76.

b) Transetherification at 132°. A mixture of 20 g of (V) and 20 g of (VI) (equimolecular amounts) was heated in a sealed tube for 75 hours in the vapors of boiling benzene. No pressure was detected upon opening the tube. In contrast to experiment (a), the reaction mixture yellowed slightly. Fractional distillation of the mixture was effected at a temperature not higher than 132° in the mass.

(IV) (4 g, yield 28.6%) was isolated from the first fraction which was collected at 64° at 150 mm after redistillation.

d_4^{20} 0.8088; n_D^{20} 1.4069; MR_D 39.92; calculated 40.26.

0.1911, 0.2350 g substance: 15.16, 18.79 ml 0.1N HCl. Found %: N 11.1, 11.2. $C_{17}H_{17}ON$. Calculated %: 10.68.

Then several intermediate fractions were isolated which were a mixture of starting and final reaction products according to the nitrogen content and boiling point. The last fraction was (VII) (5.9 g; yield 22.7%).

B.p. 130 – 133° at 12 mm; d_4^{20} 0.8187; n_D^{20} 1.4310; MR_D 76.97; calculated 77.21.

0.1501, 0.1519 g substance: 6.31, 6.45 ml 0.1N HCl. Found %: N 5.89, 5.95. $C_{15}H_{33}ON$. Calculated %: N 5.76.

Diisobutylaminomethylhexyl ether (VII), obtained by the reaction of n-hexyl alcohol, diisobutylamine, and paraformaldehyde, had the following constants:

B.p. 133−134° at 12 mm; d_4^{20} 0.8178; n_D^{20} 1.4360; MR_D 77.82.

SUMMARY

1. The analogy between the structures of dialkylaminomethylalkyl ethers (I) and formals was pointed out and it was shown that a substitution of the lighter alkoxyl residue by a heavier one occurred by the action of primary and secondary alcohols upon (I).

2. The ability of dialkylaminomethylalkyl ethers to undergo alkoxyl radical exchange reactions was shown.

3. A series of new dialkylaminomethylalkyl ethers was synthesized.

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* See Consultants Bureau Translation, page 459.

REACTION OF CARBON TETRACHLORIDE WITH ETHYL ALCOHOL

G. A. Razuvaev and Yu. A. Sorokin

The substitution of chlorine by hydrogen during the reaction of CCl_4 with organic compounds has been little studied as yet. Such reactions proceed mainly in the presence of peroxides and have a chain character. Thus, in the case of the addition of CCl_4, initiated by acetyl peroxide or benzoyl peroxide, to olefins, in addition to heat polymerization, a concurrent process occurs which breaks the chain by means of the removal of a hydrogen from the α-carbon atom by a CCl_3 radical with the formation of a poorly active allyl type radical which is incapable of prolonging the chain, and chloroform [1].

$$RCH_2-CH=CH_2 + CCl_3^{\cdot} \rightarrow CHCl_3 + R\dot{C}H-CH=CH_2$$

The substitution of chlorine by a hydrogen also occurs on the heating of saturated hydrocarbons with CCl_4 in the presence of benzoyl peroxide or teritary butyl peroxide. The hydrogen of a tertiary carbon atom is the most active, and then that of the secondary [2]

$$(CH_3)_3CH + CCl_3^{\cdot} \rightarrow CHCl_3 + (CH_3)_3C^{\cdot},$$

$$(CH_3)_3C^{\cdot} + CCl_4 \rightarrow (CH_3)_3CCl + CCl_3^{\cdot}$$

and

$$CH_3(CH_2)_3CH_2CH_3 + CCl_3^{\cdot} \rightarrow CHCl_3 + CH_3(CH_2)_3\dot{C}HCH_3,$$

$$CH_3(CH_2)_3\dot{C}HCH_3 + CCl_4 \rightarrow CH_3(CH_2)_3CHClCH_3 + CCl_3^{\cdot}.$$

However, during the reaction of CCl_4 with polychlorides (tetrachloroethane and trichloroethane) at higher temperature (400°), the latter are only dehydrogenated by atomic chlorine, while the CCl_3 radicals dimerize into hexachloroethane [3].

$$CHCl_2CHCl_2 + 2CCl_4 \rightarrow CCl_2{=}CCl_2 + 2HCl + C_2Cl_6.$$

The formation of chloroform occurs during the heating of CCl_4 with aldehydes, which are transformed into acid chlorides. The reaction proceeds in the presence of peroxides. The radicals obtained by the decomposition of peroxides, remove hydrogen from the aldehydes to give acyl radicals which react further with CCl_4. Therefore, a chain process is created [4].

$$C_6H_5COO^{\cdot} + RCHO \rightarrow C_6H_5COOH + R\dot{C}{=}O$$

$$R\dot{C}{=}O + CCl_4 \rightarrow RCOCl + CCl_3^{\cdot},$$

$$RCHO + CCl_3^{\cdot} \rightarrow CHCl_3 + R\dot{C}{=}O, \text{ etc.}$$

A reaction occurs between CCl_4 and methanol in the absence of peroxides on heating the components to 200°, with the formation of chloroform. This corresponds to the following summary equation:

$$CCl_4 + CH_3OH \rightarrow CHCl_3 + HCl + CH_2O.$$

Then secondary processes proceed with the formation of methyl chloride as a result of the reaction of hydrogen chloride with methanol, and methylal, because of the reaction of formaldehyde with methanol in the presence of HCl.

The direction of the reaction changes by the ultraviolet illumination of a mixture of CCl_4 and methanol: the CCl_3 radicals dimerize to hexachloroethane; chloroform is not found in the reaction products. The process occurs according to the summary equation [5]:

$$CH_3OH + 2CCl_4 \rightarrow CH_2O + C_2Cl_6 + 2HCl.$$

It appeared to be of interest to continue the investigation of the reaction of CCl_4 with alcohols. Ethyl alcohol was used for this purpose, and it reacted with CCl_4 in an analogous manner. The separation of the reaction mixture into two layers occurred during the thermal reaction after heating the components to 200°. The aqueous layer contained alcohol and HCl. The non-aqueous layer consisted of a mixture of chloroform, ethyl chloride, ethyl ether, paraldehyde, and unreacted CCl_4 and alcohol.

On the basis of the products obtained, it could be concluded that the primary process is the dehydrogenation of alcohol, which occurs according to the equation:

$$CH_3CH_2OH + CCl_4 \rightarrow HCl + CH_3CHO + CHCl_3$$

Then secondary processes proceed: ethyl chloride is formed by the reaction of HCl with alcohol, which then gives ethyl ether with alcohol. Acetaldehyde polymerizes into paraldehyde.

The course of the photoreaction of CCl_4 with ethyl alcohol is different: the dehydrogenation of alcohol also occurs, but only by the action of chlorine. The CCl_3 radicals do not remove a hydrogen, but dimerize into hexachloroethane. The summary reaction has the following form:

$$C_2H_5OH = 2CCl_4 \rightarrow CH_3CHO + 2HCl + C_2Cl_6$$

The hydrogen chloride does not react with the alcohol under the given conditions, and the above mentioned side reactions do not occur.

In order to prove the different courses of the thermo-and the photoreactions, the reaction between hexachloroethane and alcohol was studied. It could be supposed that hexachloroethane, dissociating into two CCl_3 radicals, would give chloroform on heating with alcohol. In this case, it could be considered that courses of the photo- and thermoreaction would be identical in the initial stage. However, the experiments conducted showed that the dehydrogenation of alcohol occurred by means of two cleaving chlorine atoms during the heating of alcohol with hexachloroethane Hexachloroethane is converted into perchloroethylene. The primary process can be represented as follows:

$$CH_3CH_2OH + C_2Cl_6 \rightarrow CH_3CHO + C_2Cl_4 + 2HCl$$

Then follow the processes given above, the formation of ethyl chloride, ether, and paraldehyde The reaction occurs at higher temperatures and is accompanied by a considerable tarring.

The thermal reaction between CCl_4 and alcohol is accelerated by the addition of a small amount of mercuric chloride, which is transformed into mercurous chloride. In the end, the same products are obtained as without the addition of mercuric chloride.

EXPERIMENTAL

Thermal reaction of CCl_4 with ethyl alcohol. 16 ml of CCl_4 (0.17 mole) and 20 ml of 98% ethyl alcohol (0.34 mole) were heated in a sealed tube for 15 hours at 200°. The reaction mixture separated into two layers, an aqueous (upper) and a non-aqueous. Products from two experiments were used for the investigation. The tubes, cooled by a mixture of ice and salt, were opened and their contents processed. 8.4 g of an aqueous and 74.2 g of a non-aqueous part were obtained. The aqueous part was a colorless liquid with a pleasant odor, which yellowed upon prolonged standing; it had an acid reaction to Congo. the non-aqueous part was a mobile, dark raspberry colored liquid with a specific ethereal odor. 7.9 g was washed out by three treatments with small portions of ice water. The wash waters were combined with the aqueous portion, the amount of HCl determined by titration (0.06 g), and the free acetaldehyde precipitated with dimedon (0.8 g; melting point of the derivative, 140°; no depression in mixed melting point). The non-aqueous part was separated into two portions by distillation: I, 52.7 g, up to 68°; II, 13.3 g, residue.

The condensate was dried and fractionated through an effective distilling column. A trap cooled with a mixture of dry ice and toluene was connected to the receiver of the column. The following fractions were obtained: 1 – 6.4 g to 25° (in trap); 2 – 3.8 g, 25.0-41.5°; 3 – 7.5 g, 41.5-62.2°; 4 – 30.8 g, 62.0-77.0°; residue 2.1 g.

Fraction 1 was ethyl chloride containing traces of acetaldehyde. The ethyl chloride was identified by conversion into ethyl mercuric chloride with m.p. 191.5°. The acetaldehyde, washed out with ice water, was identified as the dimedon derivative.

Fraction 2 was distilled, whereby 3.1 g of ethyl ether was collected at 34.1 – 35.0°.

6.7 g of chloroform boiling at 59.2 – 62.0°; d_4^{20} 1.481; n^{20} 1.440; MR 21.26; calculated 21.40, was isolated from fraction 3 after a supplementary drying with calcium chloride and distillation over P_2O_5.

Fraction 4 was distilled over P_2O_5. 29.6 g of a condensate boiling at 65.6 – 77.0° was obtained, a mixture containing mainly CCl_4. The residue (13.5 g) was distilled, first at atmospheric pressure, and then in vacuum.

The following fractions were obtained: 1 – 7.5 g, 68-98°, 2 – 3.2 g, 65-85° (at 18 mm), residue, 2.8 g, a solid glass-like, dark brown mass, readily soluble in acetone. Fraction 1 was a mixture of paraldehyde and CCl_4 which was proved by the preparation of acetaldehyde-2,4-dinitrophenylhydrazone with m.p. 167.5°. Fraction 2 was a straw-yellow viscous liquid which decolorized bromine water; it was not investigated further.

The reaction of CCl_4 with alcohol in the presence of mercuric chloride was effected with the same amounts of components. 1 g of mercuric chloride was used for each tube. The heating time (at 200°) was 15 hours. The reaction mixture also separated into two layers, and a friable precipitate of mercurous chloride crystals formed on the bottom of the tube (98% based on the mercuric chloride used). 0.1 g of HCl was found by the combined titration of the aqueous part and the wash water (from both tubes). Acetaldehyde was identified as the 2,4-dinitrophenylhydrazone (m.p. 147°). The subsequent processing of the non-aqueous part was effected in the same manner as in the previous experiments. 7.2 g of chloroform (b.p. 59.2 – 61.4°; d_4^{20} 1.478; n^{20} 1.450; MR 21.60, calculated 21.40), 5 g of ethyl chloride (identified as in the previous manner), and 3.5 g of ethyl ether (34.0 – 34.4°) were obtained.

Photochemical reaction of CCl_4 with ethyl alcohol. 16 ml of CCl_4 and 20 ml of ethyl alcohol were illuminated in a quartz apparatus by the light of a mercury-quartz lamp for 520 hours. A trap containing alkali was fitted on a glass holder with the apparatus. The reaction mixture started to separate into two layers after approximately 56 hours. The boundary of the lower layer rose and then remained at the same level (corresponding to a volume of 10.1 ml for the lower layer). The brown colored reaction mixture was washed with water, and the aqueous layer was separated. 4.8 g of HCl was found by titration, in the trap and in the aqueous layer, which corresponded to 78.6% based on the CCl_4 used for the reaction. Acetaldehyde was precipitated in the form of the dimedon derivative with m.p. 140° (0.5 g). After careful distillation of the carbon tetrachloride from the non-aqueous part, 3.1 g of hexachloroethane was isolated. The sublimed product melted at 185° (closed capillary).

Thermal reaction of hexachloroethane with ethyl alcohol. 15 g of C_2Cl_6 (0.06 mole) and 30 ml of 98% ethyl alcohol (0.51 mole) were heated in a sealed tube for 24 hours at 220°. The reaction mixture tarred badly and separated into two layers. Material from two tubes was used for the investigation, which was then processed as given above. The amount of HCl (0.4 g) was determined by titration of the aqueous layer (16.5 ml) and the wash water Acetaldehyde was identified as the 2,4-dinitrophenylhydrazone (m.p. 168°). The non-aqueous part of the reaction mixture (55.2 g) was separated from the tarry products (3.1 g) by distillation to 146°; the condensate was dried with calcium chloride, and fractionated through an effective laboratory column. The following fractions were obtained: 1 – 7.5 g, to 34° (in trap); 2 – 2.2 g, 34.0-34.6°; 3 – 20.3 g, 34.6-98.5°; 4 – 18.5 g, 98.5-145.0°; residue 3.5 g.

Fraction 1 was ethyl chloride with impurities of acetaldehyde.

Fraction 2 was ethyl ether.

Fractions 3 and 4 combined were treated with several drops of concentrated sulfuric acid with slight heating; the black aldehydic mass formed was discarded, and perchloroethylene (6 ml) was collected upon redistillation through a small effective column at 120.1 – 120.5°.

d_4^{20} 1.625; n^{20} 1.501; MR 30.05; C_2Cl_4F; calculated 30.39.

SUMMARY

1. Acetaldehyde, chloroform, and HCl were obtained upon heating carbon tetrachloride with ethyl alcohol. The reaction was accompanied by the subsequent processes forming ethyl chloride, ethyl ether, paraldehyde, and other products.

2. The photoreaction between the same components proceeded in another direction. The alcohol was dehydrogenated to acetaldehyde by one chlorine atom of the CCl_4, with the formation of hydrogen chloride. The $CCl_3^{\cdot}$ radicals were dimerized to hexachloroethane.

3. Hexachloroethane was not an intermediate product of the thermal reaction of CCl_4 with alcohol, since perchloroethylene, HCl, and acetaldehyde was formed upon heating C_2Cl_6 with ethanol.

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NITRATION OF 1-PROPYLNAPHTHALENE AND 4-NITRO-1-PROPYLNAPHTHALENE; 4-AMINO-1-PROPYLNAPHTHALENE AND SEVERAL DERIVATIVES

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The nitration reaction of 1-propylnaphthalene and its nitro- and amino- derivatives was first investigated in this study. A detailed report on the method for the preparation of 1-propylnaphthalene by the hydrogenation of 1-allylnaphthalene in the presence of platinum black is given in R. Ya. Levina and coworkers' paper [1]. In addition, the hydrogenation of 1-allylnaphthalene with a nickel catalyst [2] at high pressure has been reported in the literature. This hydrocarbon was now hydrogenated in the presence of Raney nickel without the use of high pressures.

The nitration of 1-propylnaphthalene was effected with nitric acid of various concentrations, without solvent, or in glacial acetic acid solution.

The best results were obtained by nitrating with nitric acid (d 1.40) without a solvent at 40°. In this case, a liquid mixture (yield 80%) was obtained after nitration, from which crystalline 4-nitro-1-propylnaphthalene could be isolated in a yield of 35%. The position of the nitro group in it was proved by oxidation with nitric acid in a sealed tube as a result of which 4-nitro-1-naphthoic acid was formed

After the separation of the crystalline 4-nitro-1-propylnaphthalene (see the experimental section), a liquid substance with a higher boiling point remained; upon investigation, it was shown that it was a mixture of mononitropropylnaphthalenes.

4-Nitro-1-propylnaphthalene was converted into 4-amino-1-propylnpahthalene upon catalytic reduction with hydrogen in the presence of Raney nickel; acyl derivatives and several other compounds of interest for pharmacological investigation were obtained from this compound.

EXPERIMENTAL

1-Allylnaphthalene

The preparation of 1-allylnaphthalene from naphthyl magnesium bromide and allyl bromide was reported by Fieser and Herschberg [3]; these investigators recommended the addition of the Grignard reagent to the allyl bromide, which requires a special apparatus. The order of addition of the reactant was changed.

207.2 g of 1-bromonaphthalene in 400 ml of absolute ether was added to 25 g of magnesium and heated for 2 – 3 hours. Upon cooling to room temperature, 100 ml of benzene and 121 g of allyl bromide in 200 ml of absolute benzene was added, and the mixture was heated for 2.5 hours more. After treatment of the reaction mixture with hydrochloric acid, the benzene ether layer was washed with water, then with a sodium hydroxide solution, once more with water, and dried with calcium chloride. After removal of the solvents, the substance remaining was vacuum distilled. 102.6 g (60% of the theoretical) of 1-allylnaphthalene with b.p. 134 – 135° at 11 mm was obtained.

1-Propylnaphthalene

A solution of 25 g of 1-allylnaphthalene in 150 ml of 96% ethyl alcohol and 5.5 g of nickel catalyst in 20 ml of ethyl alcohol was shaken in an atmosphere of hydrogen. Upon completion of the reaction, the purification of 1-propylnaphthalene was effected by the method of R. Ya. Levina and coworkers [1]. The yield of 1-propylnaphthalene with b.p. 119 – 120° at 17 mm was 23.5 g (93% of the theoretical). After redistillation over sodium, b.p. 134.5° at 11.5 mm; d^{20} 1.9904; n^{20}_{D} 1.5928.

4-Nitro-1-propylnaphthalene

1) 62 ml of nitric acid (d 1.40) was added at 40° over one hour to 30.9 g of 1-propylnaphthalene. After the addition of the acid, the mixture was stirred for 20-30 minutes more, and then poured into water. The acidic solution was extracted with ether. The ether solution was washed with sodium carbonate solution, then with water,

and dried with calcium chloride. The ether was removed, and substance remaining was vacuum distilled. The substance came over at 159 – 161° at 2 mm. Yield, 31.3 g (80%). A dark tarry substance was in the residue.

After many redistillations of the substance with b.p. 159 – 161° at 2 mm, a substance with b.p. 143 – 144° at 1,5 mm was collected. Yield 14.5 g.

5,030 mg substance: 0.234 ml N_2 (25.5°, 734.0 mm). 3.141 mg substance: 8.359 mg CO_2; 1.793 mg H_2O. Found %: N 6.46; C 72.57; H 6.39. $C_{13}H_{13}O_2N$. Calculated %: N 6.51; C 72.54; H 6.09.

The substance with b.p. 143 – 144° at 1.5 mm partially crystallized several hours after distillation; it was dissolved in petroleum ether, and the solution was cooled; a solid nitropropylnaphthalene crystallized upon scratching. A substance with m.p. 33 – 35° was obtained after washing with cold petroleum ether on the funnel. The substance with m.p. 33 – 35° was vacuum distilled in order to determine its boiling point; b.p. 145.5° at 1.5 mm. For analysis, the substance with m.p. 33 – 35° was recrystallized from petroleum ether; a light yellow crystalline substance with m.p. 34 – 35° was obtained; the substance was soluble in petroleum ether, alcohol and other organic solvents.

7.385 mg substance: 0.433 ml N_2 (21.0°, 732.5 mm). 0.700 mg substance: 0.381 ml N_2 (18.0°, 720.0 mm). 4.481 mg substance: 1.910 mg CO_2; 2.437 mg H_2O. Found %: N 6.56, 6.32; C 72.48; H 6.08. $C_{13}H_{13}O_2N$. Calculated %: N 6.51; C 72.54; H 6.09.

2) The nitration and subsequent processing of the product of the nitration of 40.9 g of 1-propylnaphthalene was effected as in the previous experiment. A substance with b.p. 164 – 169° at 3 mm was obtained. Yield 42.3 g (82.6%). 42.3 g of the liquid reaction product was dissolved in alcohol. Upon cooling the solution and scratching, a crystalline substance formed. After recrystallization from petroleum ether, 15.4 g (30% of the theoretical; 40% of the total mixture of nitropropylnaphthalenes) of a substance with m.p. 33 – 35° was obtained. The alcohol was distilled off from the mother liquor remaining after the removal of the substance which crystallized upon cooling the alcoholic solution. The substance remaining was vacuum distilled; it was separated into two fractions: 1 – 153-156° at 2 mm and 2 – 164-166° at 2 mm. No solid nitro compound could be formed upon dissolving each of the fractions in petroleum ether and cooling.

Upon investigation of all of the petroleum ether mother liquor from the two experiments, 4-nitro-1-propylnaphthalene and a liquid substance with b.p. 153 – 154° at 2 mm; n_D^{19} 1.6170; d^{20} 1.677., were isolated in small amounts.

10.430 mg substance: 0.600 ml N_2 (25.0°, 729.5 mm). 4.299 mg substance: 11.420 mg CO_2; 2.346 mg H_2O. Found %: N 6.33; C 72.45; H 6.10. $C_{13}H_{13}O_2N$. Calculated %: N 6.51; C 72.54; H 6.09.

3 g of the liquid substance with b.p. 153 – 154° at 2 mm and 21 ml of nitric acid (11%) were heated for 7 hours at 168 – 173° in a sealed tube. A substance with a constant melting point could not be isolated from the mixture of crystalline and tarry substances formed.

5.1 g of the substance with b.p. 153 – 154° at 2 mm, 50 ml of ethyl acetate, and 11 g of Raney nickel catalyst were shaken in an atmosphere of hydrogen. A substance with b.p. 155 – 156° at 3 mm was obtained at the end of the reaction and usual processing. The acetyl derivative obtained from this substance melted at 133.5 – 135°. No depression was found in a mixed melting point of this substance and 4-acetylamino-1-propylnaphthalene.

Oxidation of 4-nitro-1-propylnaphthalene. 2.8 g of 4-nitro-1-propylnaphthalene with m.p. 34 – 35° and 38 ml of nitric acid (11%) were heated for 6.5 hours at 168° and 1 hour at 168 – 173° in a sealed tube. 4-Nitro-1-naphthoic acid with m.p. 221.5 – 222.5° was isolated upon purification of the substance formed. A mixed melting point of this substance with 4-nitro-1-naphthoic acid obtained by another method (m.p. 223-223.5°) showed no depression (m.p. 222-223°).

4-Amino-1-propylnaphthalene

10 g of Raney nickel catalyst was added to a solution of 10 g of 4-nitro-1-propylnaphthalene* in a mixture of 50 ml of ethyl acetate and 80 ml of ethyl alcohol, and the hydrogenation was effected. At the completion of the reaction, the catalyst was filtered, and the solvent removed. The substance remaining was dissolved in ether. The ether solution was dried with potassium hydroxide. After removal of the ether, the substance was vacuum distilled B.p. 172 – 175° at 8 – 9 mm. Yield, 6.85 g (80%). Upon redistillation, the substance distilled completely at 154.5° (3 mm).

6.449 mg substance: 3.40 ml 0.01N H_2SO_4. 5.790 mg substance: 3.00 ml 0.01N H_2SO_4. 4.596 mg substance: 14.212 mg CO_2; 3.329 mg H_2O. Found %: N 7.38, 7.25; C 84.39; H 8.11. $C_{13}H_{15}N$. Calculated %: N 7.56; C 84.24; H 8.16.

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* m.p. 33-55°

4-Acetylamino-1-propylnaphthalene. 2.2 ml of acetic anhydride was added to 2.3 g of aminopropylnaphthalene in 1 ml of benzene. The crystalline substance obtained melted at 133° after two recrystallizations from aqueous alcohol; 4-acetylamino-1-propylnaphthalene dissolved in alcohol, acetone, benzene; it did not dissolve in water.

5.935 mg substance: 0.340 ml N_2 (28.0°, 728.0 mm). Found %: N 6.22. $C_{15}H_{17}ON$. Calculated %: N 6.16.

4-Benzoylamino-1-propylnaphthalene. 0.49 g of benzoyl chloride was added to a solution of 0.5 g of 4-amino-1-propylnaphthalene and 0.45 g of dimethylaniline on 10 ml dry benzene; a precipitate formed. A substance (0.75 g) was obtained after the usual processing which melted at 165-166° after recrystallization first from aqueous alcohol and then from benzene. The substance dissolved upon heating in benzene, dissolved readily in alcohol and acetone, and did not dissolve in water.

8.177 mg substance: 0.354 ml N_2 (25°, 727.0 mm). Found %: N 4.74. $C_{20}H_{19}ON$. Calculated %: N 4.84.

Ethyl ester of (1,4-propylnaphthyl)carbamic acid $C_3H_7C_{10}H_6NHCOOC_2H_5$. 0.45 g of ethyl chlorocarbonate was added to a solution of 0.5 g of 4-amino-1-propylnaphthalene and 0.45 g of dimethylaniline in 8 ml of absolute benzene, and heated for 3 hours at 40 – 50°. After the usual processing and many recrystallizations from petroleum ether, a substance with m.p. 69.5 – 70°, soluble in organic solvents, and insoluble in water, was obtained.

6.698 mg substance: 2.67 ml 0.1N H_2SO_4. Found %: N 5.58. $C_{16}H_{19}O_2N$. Calculated %: N 5.45.

Isopropyl ester of (1,4-propylnaphthyl)carbamic acid $C_3H_7C_{10}H_6NHCOOC_3H_7$-iso. 0.7 g of isopropyl chlorocarbonate in 7 ml of absolute benzene was added to a solution of 0.75 g of 4-amino-1-propylnaphthalene and 0.7 g of dimethylaniline. The m.p. was 105.5 – 106.5° after recrystallization of the substance obtained from petroleum ether. Long white needles dissolving readily in organic solvents and not soluble in water were obtained.

9.240 mg substance: 0.435 ml N_2 (23.0°, 727.0 mm). 5.130 mg substance: 0.242 ml N_2 (24.5°, 728.0 mm). Found %: N 5.19, 5.01. $C_{17}H_{21}O_2N$. Calculated %: N 5.16.

Methyl ester of (1,4-propylnaphthyl)carbamic acid $C_3H_7C_{10}H_6NHCOOCH_3$. 0.45 g of methyl chlorocarbonate was added to a solution of 0.5 g of 4-amino-1-propylnaphthalene and 0.45 g of dimethylaniline in 88 ml of absolute benzene. The reaction procedure and processing of the substance was the same as in the previous experiments. The substance obtained melted at 67 – 68° after recrystallization from petroleum ether. Shiny platelets readily dissolving in organic solvents and insoluble in water were obtained.

7.732 mg substance: 0.403 ml N_2 (25.0°, 735.0 mm). 3.089 mg substance: 8.400 mg CO_2; 1.990 mg H_2O. Found %: N 5.77; C 74.21; H 7.21. $C_{15}H_{17}O_2N$. Calculated %: N 5.76; C 74.06; H 7.04.

1,4-Propylnaphthylamide of carbomethoxysulfanilic acid $C_3H_7C_{10}H_6NHSO_2C_6H_4NHCOOCH_3$. 1.5 g of carbomethoxysulfanilic chloride was added to a solution of 1 g of 4-amino-1-propylnaphthalene in 10 ml of pyridine bases, and the solution heated on the water bath for 5 hours at 55 – 60°. At the end of the heating, the solution was poured into water; an oil separated which crystallized upon cooling and scratching. 1.6 g with m.p. 182 – 186° was obtained. M.p. 182.5 – 183° after two more recrystallizations from dichloroethane. A white crystalline substance, difficultly soluble in alcohol and insoluble in water.

0.1699 g substance: 0.0906 g $BaSO_4$. 0.1752 g substance: 0.0919 g $BaSO_4$. Found %: S 7.97, 7.78. $C_{21}H_{22}N_2O_4S$. Calculated %: S 8.02.

$C_3H_7C_{10}H_6NHSO_2C_6H_4NH_2$. 1,4-Propylnaphthylamide of sulfanilic acid. 0.55 g of (1-propylnaphthyl-4)amide of carbomethoxysulfanilic acid and 10 ml of a 13% solution of NaOH was heated for 2 hours. Upon cooling, the reaction mixture was acidified with dilute acetic acid. 0.4 g of a substance was obtained which melted at 175.5 – 176.5° after recrystallization from alcohol. The substance dissolved in alcohol and other organic solvents.

3.462 mg substance: 8.496 mg CO_2; 1.701 mg H_2O. 3.880 mg substance: 9.517 mg CO_2; 1.980 mg H_2O. Found %: C 66.97, 66.94; H 5.82, 5.71. $C_{19}H_{20}O_2N_2S$. Calculated %: C 67.04; H 5.92.

SUMMARY

1. 4-Nitro-1-propylnaphthalene was isolated upon nitration of 1-propylnaphthalene; its structure was proved.
2. 4-Amino-1-propylnaphthalene, its acyl and other derivatives were obtained.

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INVESTIGATIONS OF HYDROXYFUCHSONE DYES

XVII. CONDENSATION OF ISOMERIC NITROBENZALDEHYDES WITH GUAIACOL

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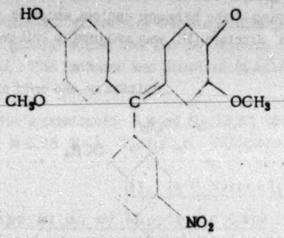
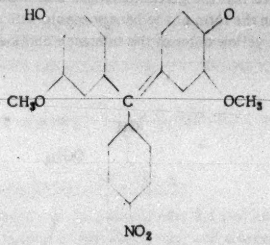
Nitro derivatives of hydroxyfuchsones have scarcely been studied. Only in one patent [1] is the preparation of 3"-nitro-3,3'-dimethoxy-4-hydroxyfuchsone hydrochloride (I) reported; however, this dye was not isolated in the free state by the authors of the patent.

The condensation of isomeric o-, m-, and p-nitrobenzaldehyde with guaiacol was conducted under conditions used in the authors' laboratory [2] for the preparation of various hydroxyfuchsones which consisted of the saturation of a mixture of the aldehyde and phenol with dry hydrogen chloride, followed by allowing this mixture to stand at room temperature.

The corresponding triphenylmethane derivatives were obtained by the condensation of m-nitrobenzaldehyde and p-nitrobenzaldehyde with guaiacol from which 3"-nitro-3,3'-dimethoxy-4-hydroxyfuchsone (I) and 4"-nitro-3,3'-dimethoxy-4-hydroxyfuchsone (II) were obtained in the form of the hydrochlorides by oxidation with nitrous oxide in amyl acetate saturated with hydrogen chloride [2].



(I)



(II)

These dyes formed, in a manner similar to the parent substance of this group, benzaurin, hydrate forms by the hydrolysis of their salts, which firmly retained water. In order to obtain these dyes in the anhydro-forms, a method was used which was applied in the authors' laboratory [3] for the preparation of methoxyfuchsone and which consisted of the heating of the hydrate form of the dye with glacial acetic acid, followed by co-distillation of the solvent and the water in vacuum. The dyes obtained crystallized readily from glacial acetic acid. The m-nitro derivative (I) was obtained in the form of orange-red crystals with m.p. 229–230° [2]. The p-nitro derivative (II) was obtained in the form of bright red crystals with m.p. 235–236°. Both dyes were soluble in mineral acids with a violet color; in alkalies they were soluble with the appearance of a blue color with a distinct greenish shade for the p-isomer.

Gold-yellow crystals with m.p. 181–182° were obtained from o-nitrobenzaldehyde upon condensation with guaiacol under the above conditions, after recrystallization from alcohol. Supposing that this substance was a usual condensation product of the triphenylmethane structure, it was oxidized in order to convert it into the corresponding fuchsone dye. However, the substance remained unchanged. Analytical determination revealed that the given compound contained chlorine which was not saponified upon heating with sodium hydroxide; the substance had the composition $C_{14}H_{10}O_3NCl$, and therefore, it was formed as the result of the condensation of 1 molecule of o-nitrobenzaldehyde with 1 molecule of guaiacol with the simultaneous chlorination of one of the benzene rings, because of the presence of the hydrogen chloride. Such an "anomalous" behavior of o-nitrobenzaldehyde upon condensation with several phenols in the presence of hydrochloric acid has previously been mentioned in the literature.

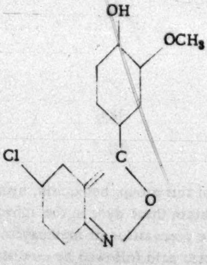
Even in 1901, Guyot and Haller [4], desiring to prepare nitrobenzaurin, conducted the condensation of o-nitrobenzaldehyde with phenol, using hydrochloric acid as the condensing agent. However, they obtained chlorohydroxyacridone instead of the desired triphenylmethane derivative, which was formed as a result of the rearrangement of the intermediately formed o-nitrodiphenylcarbinol derivative, followed by the cyclization of the acridone ring; the introduction of the chlorine, evidently, occurred during the process of the above rearrangement as a result of oxidative chlorination.

However, Zincke and Siebert [5] suggested that the substance formed during the condensation of o-nitrobenzaldehyde with phenol in the presence of hydrochloric acid was not the acridone derivative, but an anthranil. An analogously constructed compound was obtained by the condensation of o-nitrobenzaldehyde with dimethylaniline under the same conditions [6].

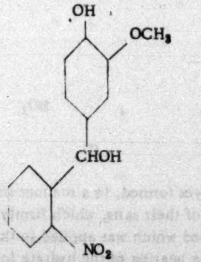
This conclusion was based on the fact that these condensation products of o-nitrobenzaldehyde with phenol or with dimethylaniline were readily transformed into diphenylketone derivatives upon reduction. Such a cleavage of the rings was rather likely with anthranils, and not very with acridones. The views of Zincke and co-workers were confirmed by Bamberger [7]. He showed that the products of the condensation of o-nitrobenzaldehyde with phenols in the presence of hydrochloric acid, were converted into amino compounds by reduction with zinc in acidic medium, which could be easily detected by diazotization and coupling with azo formers. Acridones do not open the ring during such reduction.

The above papers give apparently persuasive arguments in favor of the anthranilic structure of the above substances. Only the position of the chlorine atom in the reaction products remains unknown.

The product of the composition $C_{14}H_{10}O_3NCl$ obtained from o-nitrobenzaldehyde and guaiacol also formed an amino compound on reduction with zinc in acidic medium, the amino group in which was proven by diazotization of the product reduction, and the preparation of azo dyes with β-naphthol and N-acid. Upon this basis, it is considered that the given compound also contains the anthranil group. The latter, however, is more correctly represented in the form of the benzisoxazole with an o-quinoid grouping of the benzene nucleus, which is confirmed by the bright yellow color of the substance obtained For this reason, structure (III) was assigned to this compound:



(III)



(IV)

The formation of this compound, evidently, is due to the rearrangement of the diphenylcarbinol derivative (IV) initially formed as a result of the condensation of 1 molecule of o-nitrobenzaldehyde with 1 molecule of guaiacol. Such a rearrangement resembles that of o-nitrotoluene to anthranilic acid in its mechanism. The oxidative chlorination also occurred during this rearrangement, with the introduction of a chlorine into the o-nitroaldehyde nucleus.

EXPERIMENTAL

I. 3''-Nitro-3,3'-dimethoxy-4-hydroxyfuchsone

Preparation of the leuco base. A mixture of 21.0 g of m-nitrobenzaldehyde and 38.0 g of guaiacol (10% excess of theory) was placed into a thick-walled vessel, saturated with dry hydrogen chloride (3.5 g), and left to stand for 10 days in the cold. At the end of the reaction, the mixture solidified into a continuous crystalline monolith, which was extracted and boiled several times with a 2% sodium carbonate solution until the product did not melt upon boiling. The yield was 46.5 g (88% of the theoretical). The crude product obtained was covered with 60% alcohol overnight, the product was filtered after 12 hours, washed with 60% alcohol, and dried in a desiccator. The yield was 26.6 g (50.5% of the theoretical). The product was purified by recrystallization from 50% alcohol. The crude leuco base was also suitable for further processing. 3"-Nitro-3,3'-dimethoxy-4,4'-dihydroxytriphenylmethane was a prismatic light yellow crystalline substance which crystallized from concentrated and aqueous alcohol, acetic acid, benzene, and amyl acetate. After three recrystallizations from alcohol, m.p. 141.5°.

0.2616 g substance: 8.3 ml N_2 (20°, 768.5 mm). 0.2518 g substance: 8.05 ml N_2 (19.5°, 766.6 mm). Found %: N 3.65, 3.68. $C_{21}H_{19}O_6N$. Calculated %: N 3.69.

Preparation of the hydroxyfuchsone dye. 5.0 g of the crude condensation production, treated once with a 2% sodium carbonate solution, was dissolved in 50 ml of amyl acetate. The solution was saturated with hydrogen chloride gas, and nitrogen dioxide, obtained by the cleavage of sodium nitrite with sulfuric acid, was passed in for 2 hours with a continuous stream of hydrogen chloride, and left to stand overnight. The crystals of the dye hydrochloride which formed, were filtered after 12 hours, washed with amyl acetate and ether, and air dried. The yield was 3.3 g (68.5% of the theoretical). When the crystalline leuco base was used for the oxidation, 5.51 g of the hydrochloride (98% of the theoretical) was obtained from 5.0 g. The hydrochloride of the fuchsone was a violet crystalline substance with a greenish cast without a sharp melting point.

5.5 g of the hydrochloride was ground in a mortar with 80 ml of a 25% potassium acetate solution and 100 ml of water. The mixture was poured into a beaker and left to stand overnight. The next morning the red colored, friable precipitate of the hydrate form of the fuchsone which formed was filtered, washed with water, and dried in a desiccator; yield, 4.6 g.

4.6 g of the hydrate form was recrystallized from 60 ml of glacial acetic acid with the acetic acid solution of the dye being boiled for a long time on a sand bath. 3.0 g of the fuchsone crystallized (50.5% of the theoretical).

3"-Nitro-3,3'-dimethoxy-4-hydroxyfuchsone was a red-orange prismatic crystalline substance which crystallized from glacial acetic and and dry benzene. It melted at 229 – 229.5° after 3 recrystallizations from glacial acetic acid. The fuchsone was dissolved in aqueous solutions of acids and alkalies to give a red-violet color in acids and a blue one in alkalies.

0.2880 g substance: 8.9 ml N_2 (19.5°, 769.0 mm). 0.2520 g substance: 8.1 ml N_2 (20°, 757.0 mm). Found %: N 3.53, 3.65. $C_{21}H_{17}O_6N$. Calculated %: N 3.68.

II. 4"-Nitro-3,3'-dimethoxy-4-hydroxyfuchsone

Preparation of the leuco base. A mixture of 4.9 g of p-nitrobenzaldehyde, 9.8 g of guaiacol (20% excess), placed into a thick-walled vessel, was saturated with dry hydrogen chloride (0.7 g), and allowed to stand for 15 days in the cold; then the product was extracted and treated with boiling water. A light yellow product was obtained which was solid at ordinary temperatures but melted at 50 – 60°. It was used for the oxidation to the fuchsone.

Preparation of the hydroxyfuchsone of the dye. 5.0 g of the product treated as reported above, was dissolved in 60 ml of amyl acetate. The solution was saturated with hydrogen chloride and oxidized with nitrogen dioxide. Yield, 3.6 g of the hydrochloride (66% of the theoretical). The fuchsone hydrochloride was a dark violet crystalline substance with a gold cast, without a sharp melting point.

3.6 g of the hydrochloride was ground in a mortar with 50 ml of 25% potassium acetate solution and 80 ml of water. The solution was transferred to a beaker and left to stand overnight. The brown red precipitate of the hydrate form of the fuchsone which formed, was filtered after 12 hours, washed with water, and dried in a desiccator; yield, 3.0 g.

3.0 g of the hydrate form of the fuchsone was recrystallized from 25 ml of glacial acetic acid with the acetic acid solution of the dye being boiled for a long time on a sand bath. 1.57 g of the free fuchsone (48% of the theoretical) crystallized.

4"-Nitro-3,3'-dimethoxy-4-hydroxyfuchsone was a dark red, prismatic crystalline substance which readily crystallized from glacial acetic acid and dry benzene. The product melted at 235 – 235.5° after 2 recrystallizations from glacial acetic acid. The fuchsone dissolved in aqueous solutions of acid and alkalies to give a violet color in the acidic medium and a blue-green in alkaline.

0.2348 g substance: 7.75 ml N_2 (20°, 756.4 mm). 0.2206 g substance: 7.0 ml N_2 (19.5°, 758.6 mm). Found %: N 3.75, 3.62. $C_{21}H_{17}O_6N$. Calculated %: N 3.68.

III. Condensation of o-Nitrobenzaldehyde with Guaiacol

5.0 g of o-nitrobenzaldehyde mixed with 9.0 g of guaiacol (10% excess) was placed in a thick-walled vessel and saturated with hydrogen chloride (1.1 g). After a 3 week standing, the viscous orange colored product was extracted from the vessel and covered with 15 ml of 70% alcohol overnight; the yellow precipitate was filtered after 12 hours, washed with 70% alcohol, and dried in a desiccator. Yield, 2.92 g.

The product was a gold-yellow, prismatic crystalline substance which crystallized from glacial acetic acid, benzene, ethyl acetate, amyl acetate, and alcohol. The product melted at 181.5° after 3 recrystallizations from glacial acetic acid.

0.2 g of the product was heated with 10 ml of concentrated hydrochloric acid and a pinch of zinc dust, and filtered. The filtrate was cooled and diazotized with crystalline sodium nitrite. The excess nitrous acid was decomposed with urea, using a starch iodide paper for control. The solution of the diazonium salt was coupled with β-naphthol dissolved in 10% sodium hydroxide, and with H-acid dissolved in 10% sodium carbonate. The product of the coupling with β-naphthol had a red color, that with H-acid, a red-violet.

0.1501, 0.1505 g substance: 0.0793, 0.0794 g AgCl. 0.1298, 0.1248 g substance: 0.1114, 0.1067 g AgI. 0.1435 g substance: 6.3 ml N_2 (20°, 756.4 mm), 0.1336 g substance: 6.05 ml N_2 (19°, 768.0 mm). Found %: Cl 13.04, 13.10; OCH_3 11.34, 11.30; N 4.98, 5.23. $C_{13}H_7O_2NCl(OCH_3)$. Calculated %: Cl 12.88; OCH_3 11.25; N 5.08.

SUMMARY

The following nitro derivatives of dimethoxybenzaurin: 3"-nitro-3,3'-dimethoxy-4-hydroxyfuchsone and 4"-nitro-3,3'-dimethoxy-4-hydroxyfuchsone, were obtained by the condensation of m-nitrobenzaldehyde and p-nitrobenzaldehyde with guaiacol in the presence of hydrogen chloride, followed by the oxidation of the leuco compound formed.

A substance of the composition $C_{14}H_{10}O_3NCl$ was formed by the condensation of o-nitrobenzaldehyde with guaiacol in the presence of hydrogen chloride, and must be considered to be an anthranil derivative similar to the products obtained by the condensation of o-nitrobenzaldehyde with phenol or dimethylaniline, reported in the literature. The formation of this substance results from the rearrangement of the diphenylcarbinol derivative formed initially during the condensation, followed by the cyclization of the isoxazole ring; such a rearrangement is similar in mechanism to that of o-nitrotoluene to anthranilic acid, and proceeds in the presence of hydrogen chloride accompanied by the simultaneous chlorination of the substance.

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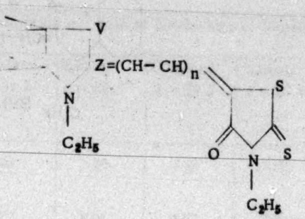
* See Consultants Bureau Translation, page a-383.

MEROCYANINE DYES, RHODANINE DERIVATIVES

V. SEVERAL TETRA- AND HEXAMETHINEMEROCYANINE DERIVATIVES OF 3-ETHYLRHODANINE

M. V. Deichmeister, I. I. Levkoev, and E. B. Lifshits

In one of the previous investigations [1], it was shown that the absorption maximum of dimethinemerocyanine derivatives of 3-ethylrhodanine (I; n = 1), as a rule, is shifted toward the longer wave lengths according to the increase in the basicity of the nitrogen heterocycle residue which is part of the dye molecule. Correspondingly, the value of the "hypsochromic shift" of the absorption maximum calculated for these dyes decreases.



V = O, S, Se, $-C(CH_3)_2$, $-CH=CH-$, $=N-CH_3$, etc; Z = hydrocarbon, or the group $CH{=}\overset{|}{C}{-}\overset{|}{C}{=}$ (in the last case the group V is absent); n = 0, 1, 2, or 3.

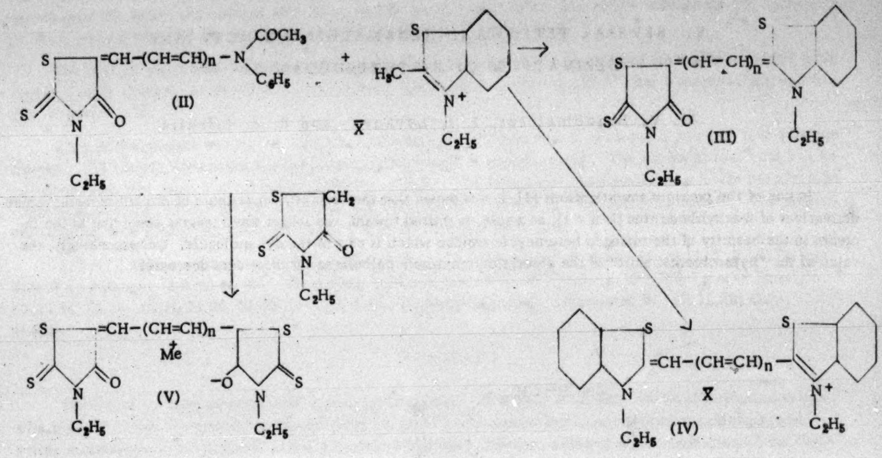
For this reason, it was suggested that the structure of similar dyes with small and moderately basic residues are more probably expressed by means of formula (I).

The relation of the color of the higher polymethinemerocyanine derivatives of rhodanine to their structure has scarcely been studied up to now. Several dyes of this series have been synthesized by Hammer [2] and Brooker [4, 5]. The latter author states that the hypsochromic shift of the absorption maximum increases upon going from the dimethine-to the tetramethinemerocyanine in the case of dyes with residues of low basicity [3, 5]. For this reason, it appeared of interest to investigate in greater detail the effect of the increase of the polymethine chain on the optical properties of these dyes and to study methods for their synthesis.

The present investigation is concerned with the synthesis of tetra-and hexamethinemerocyanine derivatives of 3-ethylrhodanine with residues of various degrees of basicity and the study of their optical properties. According to the literature, tetramethinemerocyanines are formed by the reaction of 3-ethylrhodanine with quaternary salts of 2-δ-acetanilinobutadienyl derivatives of heterocyclic nitrogen bases [2-7]. The possibility of obtaining polymethinemerocyanines by the condensation of 5-γ-acetanilinoallylidene-(II; n = 1) and 5-ε-acetanilinopentadienylidenerhodanines (II; n = 2) with quaternary salts of 2(4)-methyl substituted heterocyclic nitrogen bases [6] was also mentioned. The latter method was found to be very convenient for the preparation of tetra- and hexamethinemerocyanine derivatives of 3-ethylrhodanine, because of which this method was studied in greater detail. It was found that similar dyes with 3,3-dimethylindolenyl, benthizaolyl, and quinolenyl(2) residues were readily obtained by the condensation of 5-acetanilinoallylidene-or 5-acetanilinopentadienylidene-3-ethylrhodanine with quaternary salts of 2-methyl derivatives of the corresponding heterocyclic nitrogen bases in absolute alcoholic medium in the presence of an excess of triethylamine.

Almost in all cases during the investigation, small amounts of side dyes were isolated which were difficult to desorb from aluminum oxide and were poorly soluble in benzene. It was found that these dyes were the corresponding di- and tricarbocyanines, as for example (IV) (compare [2]).

They were formed, evidently, as a result of the rupture of the bond between the carbon atoms in the acetanilinopolymethine derivatives (compare [8]).



Tri (compare [2]) and pentamethineoxanine derivatives of 3-ethylrhodanine (V; n = 1 or 2) were also synthesized by the reaction of acetanilinoallylidene-and pentadieneylidenerhodanines (II) with 3-ethylrhodanine in pyridine in the presence of triethylamine, or in absolute ethyl alcohol in the presence of anhydrous potassium carbonate.

Salts of pentamethineoxanines (V, n = 2) were very unstable and were rapidly decomposed upon boiling with alcohol. The free dye was more stable, and it could be obtained in pure state.

The absorption curves were measured for all of the dyes synthesized, and the values of the hypsochromic shifts were calculated (in comparison to the arithmetic mean values of the absorption maxima of the corresponding dicarbocyanines and trimethineoxanines, or tricarbocyanines and pentamethineoxanines). These results are given in Table 1.

The absorption maxima of salts of mono-, tri-, and pentamethinecyanine derivatives of 3-ethylrhodanine (V) lie at 542 mμ (532), 613 mμ (613), and 714 mμ respectively. (The data of Brooker [5] for these dyes in methanol is given in the parentheses).

As it is apparent for Table 1, the intensity of the color of the dye increases upon going from the dimethinemerocyanine to the tetramethine derivative, which is greater the greater the basicity of the heterocyclic nitrogen residue. Further increase of the polymethine chain causes a much smaller bathochromic shift. Upon the introduction of one vinylene group into the polymethine chain of dimethinemerocyanine with 3,3-dimethylindolenyl and benzthiazole residues, the hypsochromic shift of the absorption maximum increases, whereas for dyes with quinolenyl-(2) residues, it decreases (from 6 to 1.5 mμ) (compare [3,5]). The hypsochromic shift increases in all cases upon going to the hexamethine derivatives; the value of this shift is greater the less basic the heterocyclic nitrogen residue.

Upon examining the results obtained, the decrease of the value of the hypsochromic shift upon the introduction of a vinylene group into the polymethine chain of dimethinemerocyanines with residues of quinoline-(2) becomes apparent. This fact can be explained by different distribution of the electron density along the polymethine chain in the molecule of the dimethinemerocyanine with a quinoline-(2) residue in comparison to dyes containing 3,3-dimethylindolenyl andbenzthiazolyl residues. In order to answer the above question, it seemed of interest to

Table 1

Heterocyclic nitrogen residue	Dimethine-merocyanines		Tetramethine-merocyanines			Hexamethine-merocyanines			Carbocyanines	Dicarbocyanines	Tricarbocyanines
	λ max. (in mμ)	Hypsochromic shift (in mμ)	λ max. (in mμ)	Hypsochromic shift (in mμ)	Vinylene shift (in mμ)	λ max. (in mμ)	Hypsochromic shift (in mμ)	Vinylene shift (in mμ)	λ max. (in mμ)		
3,3-Dimethylindolenine	503(503)	41	574(566)	49.5	71	606	124	32	546	634 (641)	745
Benzthiazole	524(526)	26	607(605)	26.5	83	636	102.5	29	558	654 (650)	763
Quinoline-2	568(565)	6	660(663)	1.5	92	687	79.5	27	606	710 (707.5)	819

Table 2

Heterocyclic nitrogen residue	Absorption maxmia of N-ethylates of dimethinemerocyanines with various heterocyclic residues (in Mμ)							
	Methanol ε = 31.2	Ethanol ε = 25.8	Propanol ε = 22.2	Butanol ε = 17.7	Chloroform ε = 4.64	Benzene ε = 2.296	Carbon-tetrachloride ε = 2.19	Hexane ε = 1.91
3,3-Dimethylindolenine	502	503	502	502	502	490	486	470
Benzthiazole	522	524	522	522	522	512	502	488
Benzoxyazole	493	492	492	493	490	480	474	460
Thiazoline	481	482	481	483	480	472	464	450
Thiazole	531	532	532	533	530	522	514	498
Pyridine-2	538	542	544	545	543	530	514	501
Quinoline-2	562	568	566	568	570	560	–	–
1-Methylbenzimidazole	508	511	512	513	517	511	–*	–*

investigate the change of the position of the absorption maxima of dimethine merocyanine derivatives of 3-ethylrhodanine (I, n = 1) in various solvents, the polarity of which, as it is known, noticeably effects the electronic structure, and therefore, the color of the intraionoidic dyes [9-13]. The data obtained are given in Table 2.

As it is apparent from Table 2, upon going from methanol to less polar solvents, the absorption maxima of dimethinemerocyanines with residues of small and moderate basicity is gradually shifted toward the lower wave lengths. In cases of dyes with pyridine, quinole, and 1-methylbenzimidazole residues, a bathochromic shift of the absorption maximum first occurs, and then, the increase of the color. These results confirmed the previous suggestion [1] that the electron density is gradually equalized along the polymethine chain in the molecule with the increase of the basicity of heterocyclic residue for the dyes investigated, as well as for the derivatives of 3-hydroxythionaphthene [12]. The structures of the dimethinemerocyanines with pyridine, quinoline, and 1-methylbenzimidazole residues in ethyl alcohol, evidently, are more correctly expressed by an intraionoidal formula, for example (VI).

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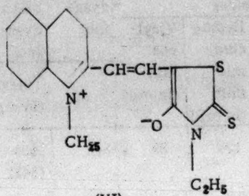
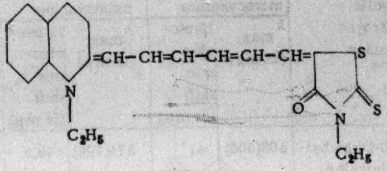
[*] In carbon tetrachloride and hexane, the color rapidly disappeared.



(VI)



(VII)

From this point of view, the generalities established for tetra-and hexamethinemerocyanines become more comprehensible.

Upon the increase of the internal chain of the merocyanines, their polarity decreases, and in all cases, the electronic shift from the nitrogen atom along the polymethine chromophore gradually decreases. In the dyes investigated containing indolenine and benzthiazole residues (in ethyl alcohol), the distribution of the electron density along the chain becomes less and less equalized, which is confirmed by the subsequent increase of the values of the hypsochromic shift of the absorption maxima. In the case of the highly polar quinomerocyanine, upon going from the di- to the tetramethine derivatives in ethyl alcohol, on the other hand, a more equivalent distribution of the electron density along the chain is attained, which upon further increase in the length of the chromophore is again broken because of which the structure of hexamethinemerocyanines in ethyl alcohol can be expressed by formula (VII). For this reason, the value of the hypsochromic shift of the absorption maximum in this group of dyes at first decreases and then increases once more.

EXPERIMENTAL

3-Ethyl-5-γ-acetanilinoallylidenerhodanine [2,6]. It was prepared by heating 0.32 g of 3-ethylrhodanine with 0.52 g of malonaldehyde dianil hydrochloride in 3 ml of acetic anhydride for 1 hour. The precipitate which formed was filtered after 12 hours, and washed with water and alcohol. Weight, 0.54 g; m.p., 215 – 217°. The yield was 0.45 g (67.7%)* after recrystallization from ethyl alcohol (1 g from 600 ml). Dark red, shiny prisms with m.p. 224 – 225° (with decomposition) (225.5 – 226.5° [6]).

Found %: N 8.36. $C_{16}H_{16}O_2N_2S_2$. Calculated %: N 8.42.

3-Ethyl-5-ε-anilinopentadienylidenerhodanine [6]. A mixture of 0.16 g of 3-ethylrhodanine, 0.28 g of glutaconaldehyde dianil hydrochloride, 2 ml absolute ethyl alcohol, and 0.1 g triethylamine were heated for 5 minutes on the boiling water bath. The precipitate which formed was filtered after 6 hours and washed with alcohol. Weight, 0.23 g; m.p. 192 – 193°. The yield was 0.2 g (63.2%) after recrystallization from ethyl alcohol (1 g from 120 ml). Blue-violet platelets with m.p. 193° (with decomposition).

Found %: N 8.97. $C_{16}H_{16}ON_2S_2$. Calculated %: N 8.85.

3-Ethyl-5-ε-acetanilinopentadienylidenerhodanine [6]. A solution of 0.23 g of 3-ethyl-5-ε-anilinopentadienylidenerhodanine in 7 ml of acetic anhydride was refluxed for 5 minutes in a flask. The precipitate which formed upon cooling was filtered after 12 hours and washed with water and alcohol. Weight, 0.18 g; m.p. 186 – 188°. The yield was 0.16 g (44.7%) after recrystallization from ethyl alcohol (1 g from 75 ml). Brownish shining platelets with m.p. 190 – 191° (with decomposition).

Found %: N 7.81. $C_{18}H_{18}O_2N_2S_2$. Calculated %: N 7.81.

3-Ethyl-5-[δ-(3'-ethylbenzthiazolinylidene-2')-butenylidene]-thiazolidinethione-(2)-one-(4) [2,4,7]. A mixture of 0.32 g of 3-ethyl-5-γ-acetanilinoallylidenerhodanine, 0.44 g of 2-methylbenzthiazole ethiodide, 20 ml of absolute ethyl alcohol, and 0.31 g of triethylamine was boiled for 30 minutes. The precipitate which formed was filtered and washed with alcohol. Weight, 0.32 g; m.p. 211 – 214° (with decom-

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[*] The yield here and subsequently is expressed in percent of the theoretical.

position). The product was boiled with 40 ml of ethyl alcohol, the insoluble residue was filtered, and recrystallized from 30 ml of benzene Yield, 0.14 g (37.4 %); m.p. 238 − 239° (with decomposition). For final purification, a benzene solution of the dye was filtered through a layer of aluminum oxide, upon which a small amount of a blue side product was strongly adsorbed. The benzene solution was evaporated in vacuum until the beginning of crystallization, the dye was filtered and washed with alcohol. Weight, 0.1 g. Dark blue needles with m.p. 238 − 239° (with decomposition) (239 − 241° [4], 238° [2]).

Found %: N 7.29. $C_{18}H_{18}ON_2S_3$. Calculated %: N 7.48.

0.11 g of a substance was isolated from the wash alcohol, which was obtained in the form of green shiny needles with m.p. 249 − 250° after three boilings with benzene and recrystallizations from methyl alcohol.

The absorption curve in ethyl alcohol, as well as the position of the absorption maximum (at 654 mμ) of the given product and those of 3,3'-diethylthiadicarbocyanine iodide coincided completely.

3-Ethyl-5[ζ-(3'-ethylbenzthiazolinylidene-2')-hexadienylidene]-thiazolidinethione-(2)-one-(4) [4, 6]. It was prepared by heating a mixture of 0.35 g of 3-ethyl-5-ε-acetanilinopentadienylidenerhodanine, 0.6 g of 2-methylbenzthiazole ethiodide, 10 ml of absolute ethyl alcohol, and 0.42 g of triethylamine for 20 minutes. Weight, 0.2 g; m.p. 209 − 210° (with decomposition). The yield was 0.14 g (35%) after washing with boiling ethyl alcohol (2 times with 25 ml), crystallization from benzene (1 g from 500 ml); m.p. 223 − 224° (with decomposition). The weight of the purified merocyanine was 0.1 g after removal of the blue-green side product upon aluminum oxide.

Green needles with m.p. 223 − 224° (with decomposition) (231 − 233° [4]).

Found %: N 7.04. $C_{20}H_{20}ON_2S_3$. Calculated %: N 6.99.

0.08 g of a substance separated upon standing from the wash alcohol, which, upon boiling with benzene and recrystallization from ethyl alcohol, was obtained in the form of green needles with a golden sheen with m.p. 210 − 212° (m.p. of 3,3'-diethylthiatricarbocyanine iodide is 210 − 212° [11]). The sensitization maximum was 810 mμ.

3-Ethyl-5-[δ-(1'-ethyl-3',3'-dimethylindolinylidene-2')-butenylidene]-thiazolidinethione-(2)-one-(4). [5]. A mixture of 0.32 g of 3-ethyl-5-γ-acetanilinoallylidenerhodanine, 0.31 g of 2,3,3-trimethylindolinine ethiodide, 2 ml of butanol, 1 ml of pyridine, and 0.1 g of triethylamine was heated for 2.5 hours at 120°. On the following day, the precipitate which formed was filtered and washed with alcohol. Weight 0.19 g; m.p. 155 − 157° (with decomposition). The yield was 0.13 g (38.8%) after recrystallization from ethyl alcohol (1 g from 90 ml). For final purification, a benzene solution of the dye was filtered through a layer of aluminum oxide upon which the blue-violet side product was adsorbed. 0.08 g of the substance in the form of grey, shiny prisms with m.p. 166 − 167° (with decomposition) (176 − 178° [5]) was obtained from the benzene solution after evaporation in vacuum.

Found %: N 7.06. $C_{21}H_{24}ON_2S_2$. Calculated %: N 7.28.

3-Ethyl-5-[ζ-(1'-ethyl-3',3'-dimethylindolinylidene-2')-hexadienylidene]-thiazolidinethione-(2)-one-(4). A mixture of 0.7 g of 3-ethyl-5-ε-acetanilinopentadienylidenerhodanine, 2.1 g of ethyl-p-tolylsulfonate of 2,3,3-trimethylindolinine, 4 ml butanol, 2 ml pyridine, and 0.42 g of triethylamine were heated for 2 hours at 130°. 3 ml of ethyl alcohol was then added, and the liquid cooled with ice. The dye which precipitated was filtered after 12 hours and washed with alcohol. Weight, 0.17 g; m.p. 169 − 172° (with decomposition). After recrystallization from propanol (1 g from 100 ml) and filtration through a layer of aluminum oxide, with which the removal of impurities of a blue side product was accomplished, 0.14 g of a substance (17%) was obtained in the form of green, shiny prisms with m.p. 182° (with decomposition).

Found %: N 6.96. $C_{23}H_{26}ON_2S_2$. Calculated %: N 6.82.

3-Ethyl-5[δ-(1'-ethyldihydroquinolidene-2')-butenylidene]-thiazolidinethione-(2)-one-4 [2, 5]. A mixture of 0.32 g 3-ethyl-5-γ-acetanilinoallylidenerhodanine, 0.6 g of quinaldine ethiodide, 8 ml of absolute ethyl alcohol, and 0.42 g of triethylamine were boiled for 30 minutes. The precipitate which formed was filtered after 6 hours and washed with alcohol. Weight 0.32 g; m.p. 202 − 212° (with decomposition). After boiling with 50 ml of ethyl alcohol, the insoluble residue was recrystallized from benzene (1 g from 500 ml). Yield 0.08 g (21.7%); m.p. 253 − 255° (with decomposition). For a final purification, a benzene solution of the dye was filtered through a layer of aluminum oxide, upon which an impurity of green side product was adsorbed. 0.4 g of a substance was obtained in the form of blue prisms with m.p. 253 − 255° (with decomposition) (253 − 255° [5], 270° [2]).

Found %: N 7.50. $C_{20}H_{20}ON_2S_2$. Calculated %: N 7.60.

3-Ethyl-5-[ζ-(1'-ethyldihydroquinolylidene-2')-hexadienylidene]-thiazolidinethione-(2)-one-(4). A mixture of 0.35 g of 3-ethyl-5-ε-acetanilinopentadienylidenerhodanine, 0.6 g of quinaldine ethiodide, 10 ml of absolute ethyl alcohol, and 0.42 g of triethylamine were boiled for 30 minutes. The dye which precipitated was filtered after 6 hours and washed with alcohol. Weight 0.35 g; m.p. 191° (with decomposition). The yield was 0.16 g (40.5%) after washing the dye with 10 ml of boiling alcohol and recrystallization of the residue from 155 ml of ethyl alcohol and then from a mixture of ethyl alcohol and benzene (1:1) (1 g from 625 ml); m.p. 226 – 227° (with decomposition). The final purification of the dye was accomplished by filtration through aluminum oxide, whereby small impurities of a green side product were removed. Green shiny prisms with m.p. 226 – 227° (with decomposition).

Found %: N 6.90. $C_{22}H_{22}ON_2S_2$. Calculated %: N 7.10.

3-Ethyl-5-[3'-ethyl-4'-hydroxythiazolinthion-(2)-yl-5'-allylidene]-thiazolidinethione-(2)-one-(4) [2, 7]. A mixture of 0.66 g of 3-ethyl-5-γ-acetanilinoallylidenerhodanine, 0.64 g of 3-ethylrhodanine, 8 ml of pyridine, and 0.82 g of triethylamine was heated for 2 hours at 130°. The cooled reaction solution was treated with 150 ml of ether. The precipitate which formed was filtered after 12 hours and washed with ether. Weight, 0.3 g; m.p. 156 – 157°. For purification, the triethylammonium salt was recrystallized from aqueous alcohol (3:1) (1 g from 60 ml). Yield 0.2 g (21.9%). Golden platelets with m.p. 170 – 171° (with decomposition).

Found %: N 9.23. $C_{19}H_{29}O_2N_3S_4$ Calculated %: N 9.12.

15 ml of concentrated hydrochloric acid (d 1.18) was added to a solution of 0.46 g of the triethylammonium salt in 100 ml of 50% aqueous alcohol. The precipitate which formed was filtered, washed with water and alcohol, and then crystallized from glacial acetic acid (1 g from 85 ml) after drying. Yield, 0.15 g (41.8%). Yellow needles with m.p. 128 – 130° (with decomposition). (According to Hamer and Winton, it liquifies at 160° and decomposes at 210° [2]).

Found %: N 7.69. $C_{13}H_{14}O_2N_2S_4$ Calculated %: N 7.81.

3-Ethyl-5-[3'-ethyl-4'-hydroxythiazolinthion-(2)-yl-5'-pentadienylidene]-thiazolidinethione-(2)-one-(4). A mixture of 0.33 g of 3-ethyl-5-ε-acetanilinopentadienylidenerhodanine, 0.32 g of 3-ethylrhodanine, 5 ml of absolute ethyl alcohol, and 0.27 g of anhydrous potassium carbonate was boiled for 15 minutes. The unreacted potassium carbonate was filtered, and 50 ml of absolute ether was added to the filtrate. The precipitated potassium salt was filtered on the following day and washed with ether. Weight 0.36 g; m.p 146-150° (with decomposition). It was readily soluble in alcohol, noticeably in water, and difficultly in ether. Upon boiling with alcohol, the salt of the dye was decomposed. 2 ml of glacial acetic acid was added to a suspension of 0.42 g of the above salt in 100 ml of water. The flocculent precipitate was filtered and washed with water and alcohol. Weight, 0.32 g; m.p. 135 – 147°. The yield was 0.14 g (36.4%) after three recrystallizations from glacial acetic acid (1 g from 20 ml). Red brown needles with m.p. 168 – 170° (with decomposition). It was very readily soluble in benzene and ether, and almost insoluble in ethyl alcohol.

Found %: N 7.48. $C_{15}H_{16}O_2N_2S_4$ Calculated %: N 7.28.

The authors wish to express their deepest gratitude to S. V. Natanson for a series of valuable suggestions and advice.

SUMMARY

1. The syntheses of several tetra- and hexamethinemerocyanine derivatives of 3-ethylrhodanine, as well as the corresponding tri- and pentamethineoxanines was effected.

2. The absorption spectra of eight dimethinemerocyanine derivatives of 3-ethylrhodanine, differing in the nature of the nitrogen heterocycle residue, were measured in various solvents.

3. On the basis of the investigation of the absorption spectra of the merocyanine derivatives of 3-ethylrhodanine, it was shown that the distribution of the electron density in their chromophores can vary considerably, in relation to the basicity of the heterocyclic residues and the length of the internal polymethine chain.

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STUDY OF THE SULFONATION REACTION

XXXIII. EQUILIBRIUM BETWEEN SULFONIC ACIDS AND THEIR ACID CHLORIDES

A. A. Spryskov and Yu. L. Kuzmina

The equilibrium between various mono- and polysulfonic acids on the one hand, and their acid chlorides, on the other, was previously studied by the authors [1,2] in a medium consisting of a mixture of sulfuric and chlorosulfonic acids, which was established according to the equation:

$$RSO_2Cl + H_2SO_4 \rightleftharpoons RSO_3H + HSO_3Cl.$$

The results of the study of the equilibrium between sulfonic acids and their acid chlorides containing various functional groups, carboxylic, nitro, and a second sulfonic, in the benzene nucleus are reported below.

Equilibrium between m-nitrobenzenesulfonic derivatives. m-Nitrobenzenesulfonyl chloride, recrystallized from glacial acetic acid, with m.p. 61.5 – 62°, was dissolved in a mixture of sulfuric and chlorosulfonic acids of various composition. The solutions were kept over phosphorus pentoxide for 10 hours at 80 ± 0.5°. After pouring onto ice, the acid chloride was filtered, washed, dried, and weighed. The results of experiment 172, given in Table 1, show that even after 3 hours of standing, the system was close to the equilibrium composition. The chloride isolated from the equilibrium mixture had a m.p. of 61.5 – 62°.

TABLE 1

Composition of the Equilibrium between m-Nitrobenzenesulfonic Acid and Its Acid Chloride at 80°

Expt. No.	Moles used per mole of chloride		Time (in hours)	Chloride obtained (in % of that used)	Equilibrium constant K
	H_2SO_4	HSO_3Cl			
174	1.36	3.54	10	85.5	0.52
168	1.48	2.14	10	78.7	0.50
169	1.92	2.07	10	74.9	0.47
172	3.06	1.52	3	56.0	
			6	58.7	0.51
			10	58.9	0.51
166	3.31	0.72	10	47.0	0.51
173	4.91	0.82	10	38.0	0.55
				Average	0.51

If for 1 mole of the acid chloride, m moles of sulfuric acid and n moles of chlorosulfonic acid are taken, then after achieving equilibrium according to the equation:

$$\begin{array}{ccccccc} RSO_2Cl & + & H_2SO_4 & \rightleftharpoons & RSO_3H & + & HSO_3Cl \\ 1-x & & m-x & & x & & n+x \end{array} \qquad (I)$$

the equilibrium constant can be calculated:

$$K = \frac{[x][n+x]}{[1-x][m-x]} \qquad (II)$$

The experimental results showed that the equilibrium constant kept practically a constant value at various ratios of sulfuric and chlorosulfonic acids.

The amount of sulfonic acid in the equilibrium mixture is calculated according to the formula:

$$x = \frac{n + K = Km \pm \sqrt{(n + K + Km)^2 - (4K - 1)\,Km}}{2\,(K - 1)} \qquad (III)$$

Table 2 gives the amount of the acid chloride (1 – x), calculated according to formula (III), and the values found experimentally.

Comparison of the results shows that the difference between the calculated and experimentally found amounts of acid chloride in the equilibrium mixture do not exceed 1.4%.

TABLE 2

Equilibrium between m-Nitrobenzenesulfonic Acid and Its Acid Chloride

Expt. No.	Sulfonyl chloride in the mixture (in % of that taken)	
	Found	Calculated
174	85.5	85.6
168	78.7	78.5
169	74.9	73.5
172	58.8	58.8
166	47.0	47.0
173	38.0	39.4

Equilibrium between m-sulfobenzoic acid and its chloride. The chloride of m-sulfobenzoic acid was recrystallized from dichloroethane until a m.p. of 133–134.5° was attained. Experiments on the study of the equilibrium were effected in the same manner as those reported for nitrobenzenesulfonic acid by keeping the mixture at 80° for 10 hours. The chloride isolated from the equilibrium mixture had a m.p. of 127–130°. The decrease in the melting point of the chloride resulted from the partial hydrolysis of the moist substance during its drying in the desiccator over sodium hydroxide. The melting point of the pure chloride was decreased in the same manner after moistening and drying.

The experimental results given in Table 3 made it possible to find the equilibrium constant according to formula (II), and to find the amount of chloride in the mixture, according to formula (III) by means of its value, equal to 1.22, for comparison with that isolated experimentally.

TABLE 3

Equilibrium between Sulfobenzoic Acid and Its Acid Chloride at 80°

Expt. No.	Moles used per mole of chloride		Chloride isolated (in % of that used)	Equilibrium, constant K	Chloride in the mixture calculated according to formula (III) (in % of that used)
	H_2SO_4	HSO_3Cl			
204	1.62	4.05	69.8	1.43	72.4
207	1.59	3.37	69.7	1.24	70.1
205	2.01	2.99	62.4	1.27	62.7
201	2.93	2.70	51.6	1.22	51.6
202	3.77	1.73	38.6	1.19	37.9
203	3.96	1.26	36.6	0.99	32.5
			Average	1.22	

Equilibrium between 2,4-toluenedisulfonic derivatives. The chloride of 2,4-toluenedisulfonic acid was recrystallized from ether until a m.p. of 52° was attained. Experiments on the study of the equilibrium were conducted in the same manner as for nitrobenzenesulfonic acid by keeping the mixture at 80° for 10 hours. The chloride isolated from the equilibrium mixture had a m.p. of 52°. The experimental results are given in Table 4. As with the above, the amount of chloride in the mixture was calculated from the equilibrium constant according to formula (III) and compared with that found experimentally (see Table 4).

TABLE 4

Equilibrium between 2,4-Toluenedisulfonic Acid and Its Acid Chloride at 80°

Expt. No.	Moles used per mole of chloride		Chloride isolated (in % of that used)	Equilibrium constant K	Chloride in the mixture calculated according to formula (III) (in % of that used)
	H_2SO_4	HSO_3Cl			
192	1.05	4.23	86.6	0.74	84.5
188	1.92	3.10	71.8	0.80	70.1
198	2.45	3.20	63.7	1.00	65.2
189	2.92	2.25	57.9	0.77	55.0
190	3.33	1.83	44.7	1.06	48.0
191	3.70	2.00	44.0	1.04	47.1
			Average	0.90	

As previously reported [2], the equilibrium in this case is established according to the equation:

$$CH_3C_6H_3(SO_2Cl)_2 + H_2SO_4 \rightleftharpoons$$

$$CH_3C_6H_3(SO_2Cl)(SO_3H) + HSO_3Cl,$$

i.e., the sulfonic acid sulfonyl chloride is formed, which can be further transformed into the disulfonic acid. For this reason, x corresponds to the number of moles of the disulfonyl chloride transformed into the sulfonic acid sulfonyl chloride.

A total of 7 cases of equilibrium between sulfonic acids and their acid chlorides have been studied by the authors [1, 2]. A comparison of results obtained is given below. If, according to equation (I), 1 mole of sulfuric acid was used per mole of the chloride, then the amount of the chloride transformed into the sulfonic acid will be about 50%, with a variation of 8% in one or the other direction, as is shown in Table 5.

TABLE 5

Equilibrium between Sulfonic Acids and Their Acid Chlorides at Equimolar Ratios of the Chloride to Sulfuric Acid

Acid chlorides	K	Amount transformed into the sulfonic acid (in%)
m-Nitrobenzenesulfonyl chloride	0.51	41.7
p-Dichlorobenzenesulfonyl chloride	0.67	45.0
p-Toluenesulfonyl chloride	1.18	52.1
Chloride of m-sulfobenzoic acid	1.22	52.5
2,4-Toluenedisulfonyl chloride	0.90	48.7
m-Benzenedisulfonyl chloride	1.33	53.6
1,3,5-Naphthalenetrisulfonyl chloride	1.90	57.9

The values of the constants for di- and trisulfonic acids, as a rule, are greater than for the monosulfonic derivatives.

SUMMARY

The equilibria between m-nitrobenzenesulfonic acid and its acid chloride, m-sulfobenzoic acid and its acid chloride, and 2,4-toluenedisulfonic acid and its acid chloride were studied in a medium consisting of sulfuric and chlorosulfonic acids at 80°. The equilibrium constants found were equal to 0.51, 1.22, and 0.90, respectively.

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The ratio of the constants for the sulfonic acids ... sulfonic, ... for the unsubstituted ...

SUMMARY

... sulfonic acid and its acid chloride, α-naphthalenesulfonic acid and its acid chloride, and ...-benzenesulfonic acid and its acid anhydride ... studied in a medium consisting of sulfuric and ... acids ... The ... constants found ... equal to ..., 1.22, and 0.85, respectively.

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The ... Institute ... of Technology and the ... Institute of ...

Table ...

... between the ... sulfonic acids and their ... chloride ... sulfuric acid

...	...	...
m-Nitrobenzenesulfonyl chloride	[illegible]	[illegible]
...-Nitrobenzenesulfonyl chloride	[illegible]	[illegible]
p-Toluenesulfonyl chloride	[illegible]	[illegible]
... of ...benzenesulfonic acid	[illegible]	[illegible]
...benzenesulfonyl chloride	[illegible]	[illegible]
...-benzenesulfonyl chloride	[illegible]	[illegible]
α-Naphthalenesulfonyl chloride	[illegible]	[illegible]

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ORGANIC INSECTOFUNGICIDES

XVI. SYNTHESIS OF SUBSTITUTED ESTERS OF THIOPHOSPHORIC ACIDS CONTAINING VARIOUS FUNCTIONAL GROUPS IN THE AROMATIC RADICAL

M. L. Galashina and N. N. Melnikov

Recently it was shown that the introduction of a simple substituent such as a halide and alkoxyl into the aliphatic radicals of one of the more active insecticides, diethyl-4-nitrophenylthiophosphate, leads to a decrease in insecticidal activity of the compound [1]. It appeared of undoubted interest to study the effect of the introduction of various substituents into the aromatic radical of dialkylarylthiophosphates on the insecticidal activity.

The synthesis of alkylarylthiopsphates containing alkoxyl, halide, thiocyano, and alkoxy and halide groups at the same time in the aromatic radical is reported in the present communication. The synthesis of alkoxyaryldialkylthiophosphates is of interest because of structural resemblance of the esters of alkylresorscin with the known preparation "Potazan", which has found application in agriculture [2]. The compounds obtained and their properties are given in the Table.

Almost all of the compounds given in the Table are not reported in the literature; diethyl-4-methoxyphenylthiophosphate is the exception, whose synthesis has been given in entomological literature [3].

The synthesis of the compounds given in the Table was effected by means of the following reactions:

$$PSCl_3 + 2ROH \longrightarrow (RO)_2PSCl + 2HCl$$

$$(RO)_2PSCl + R'OC_6H_4ONa \longrightarrow (RO)_2PSOC_6H_4OR' + NaCl$$

Tests of the dialkylarylthiophosphates conducted upon grain weevils and harmful beetles, showed that the insecticidal activity of dialkylalkoxyphenylthiophosphates was destroyed with the increase of the molecular weight of the alkoxy radical (starting with propyl).

A decrease of the insecticidal activity also occurs with the increase of the molecular weight of the ester aliphatic radical. It is interesting that the introduction of the thiocyano group in place of the nitro group sharply decreases the insecticidal activity of the compounds, while the introduction of the thiocyano group into the molecule of simple ester increases the insecticidal activity of the compounds sharply. The introduction of a halide into the dialkylalkoxyphenylthiophosphates increases the insecticidal activity of the compounds somewhat. All of the compounds given in the Table were found to be less active than diethyl-4-nitrophenylthiophosphate.

EXPERIMENTAL

The preparation of the dialkylarylthiophosphates was conducted under conditions reported in one of the previous communications [4]. An equimolecular amount of the dialkylchlorothiophosphate was added gradually with efficient stirring to the dry phenol wetted with chlorobenzene to which 1-2 drops of pyridine were added initially. The reaction mixture was then kept for several hours at 110-130°. The sodium chloride was filtered after the end of the reaction and the cooling of the reaction mixture, the filtrate washed with sodium hydroxide and water, and

Experiment No.	Name and Formula	Boiling point		d_4^{20}	n_D^{20}	Amount of phosphorous (in %)		Yield (in % of the theoretical)
		C	mm			Found	Calculated	
1	Diethyl-2-methoxyphenylthiophosphate $(C_2H_5O)_2PSOC_6H_4OCH_3$-(2)	170-174	8	1.1672	1.5990	10.90, 11.43	11.23	24
2	Diethyl-3-methoxyphenylthiophosphate $(C_2H_5O)_2PSOC_6H_4OCH_3$-(3)	97	0.02	1.1483	1.5050	11.35, 11.50	11.23	56
3	Diethyl-3-ethoxyphenylthiophosphate $(C_2H_5O)_2PSOC_6H_4OC_2H_5$-(3)	170-180	8	1.1288	1.5045	11.20, 11.06	10.7	21
4	Diethyl-3-propyloxyphenylthiophosphate $(C_2H_5O)_2PSOC_6H_4OC_3H_7$-(3)	170-180	8	1.1020	1.5038	10.1, 9.8	10.2	26
5	Diethyl-3-butyloxyphenylthiophosphate $(C_2H_5O)_2PSOC_6H_4OC_4H_9$-(3)	140-150	0.35	1.1001	1.5028	9.7, 9.4	9.75	17
6	Diethyl-3-benzyloxyphenylthiophosphate $(C_2H_5O)_2PSOC_6H_4OCH_2C_6H_5$-(3)	140-145	0.05	1.1645	1.5620	8.3, 8.5	8.8	25
7	Dipropyl-2-methoxyphenylthiophosphate $(C_3H_7O)_2PSOC_6H_4OCH_3$-(2)	117	0.05	1.1288	1.5120	9.92, 10.10	10.19	24
8	Dipropyl-3-methoxyphenylthiophosphate $(C_3H_7O)_2PSOC_6H_4OCH_3$-(3)	130-150	3	1.1106	1.4942	10.56, 10.36	10.19	18
9	Dipropyl-3-ethoxyphenylthiophosphate $(C_3H_7O)_2PSOC_6H_4OC_2H_5$-(3)	110-118	0.05	1.0949	1.4920	9.65, 9.80	9.75	18
10	Dipropyl-3-propyloxyphenylthiophosphate $(C_3H_7O)_2PSOC_6H_4OC_3H_7$-(3)	120-146	0.35	1.0790	1.4995	9.15, 8.90	9.28	25
11	Dipropyl-3-butyloxyphenylthiophosphate $(C_3H_7O)_2PSOC_6H_4OC_4H_9$-(3)	136-141	0.05	1.0754	1.5040	8.76, 8.50	8.96	14
12	Diethyl-4-methoxyphenylthiophosphate $(C_2H_5O)_2PSOC_6H_4OCH_3$-(4)	117-122	0.1	1.1910	1.5180	10.75, 11.00	11.23	46
13	Diethyl-4-ethoxyphenylthiophosphate $(C_2H_5O)_2PSOC_6H_4OC_2H_5$-(4)	135-140	0.1	1.1400	1.5140	10.70, 10.80	10.73	23
14	Diethyl-4-propyloxyphenylthiophosphate $(C_2H_5O)_2PSOC_6H_4OC_3H_7$-(4)	136	0.3	1.1086	1.5080	10.55, 10.70	10.19	22
15	Diethyl-4-butyloxyphenylthiophosphate $(C_2H_5O)_2PSOC_6H_4OC_4H_9$-(4)	153	0.2	1.0905	1.5082	9.30, 9.25	9.75	46
16	Diethyl-2-bromo-4-ethoxyphenylthiophosphate $(C_2H_5O)_2PSOC_6H_3Br$-(2)-OC_2H_5-(4)	142-150	0.02	1.3596	1.5410	8.00, 8.00	8.40	20
17	Diethyl-2-chloro-4-ethoxyphenylthiophosphate $(C_2H_5O)_2PSOC_6H_3Cl$-(2)-OC_2H_5-(4)	110-126	0.15	1.2391	1.5285	9.16, 9.42	9.56	11
18	Diethyl-4-thiocyanophenylthiophosphate $(C_2H_5O)_2PSOC_6H_4CNS$-(4)	130	0.04	1.2121	1.5510	10.63, 10.25	10.47	10
19	Dimethyl-3-ethoxyphenylthiophosphate $(CH_3O)_2PSOC_6H_4OC_2H_5$-(3)	100-107	0.02	1.1970	1.5280	11.53, 11.37	11.82	18
20	Dipropyl-4-methoxyphenylthiophosphate $(C_3H_7O)_2PSOC_6H_4OCH_3$-(4)	124	0.07	1.1201	1.5100	10.30, 10.15	10.43	48
21	Dipropyl-4-ethoxyphenylthiophosphate $(C_3H_7O)_2PSOC_6H_4OC_2H_5$-(4)	112-120	0.025	1.0956	1.5070	9.50, 9.35	9.75	52
22	Dipropyl-4-propyloxyphenylthiophosphate $(C_3H_7O)_2PSOC_6H_4OC_3H_7$-(4)	148-150	0.2	1.0221	1.4970	9.75, 9.90	9.33	10
23	Dipropyl-4-butyloxyphenylthiophosphate $(C_3H_7O)_2PSOC_6H_4OC_4H_9$-(4)	112-120	0.025	1.0082	1.4950	8.75, 8.60	8.96	30
24	Dipropyl-2-bromo-4-ethoxyphenylthiophosphate $(C_3H_7O)_2PSOC_6H_3Br$-(2)-OC_2H_5-(4)	136-140	0.05	1.3113	1.5290	8.2, 8.2	7.80	35
25	Dipropyl-2-chloro-4-ethoxyphenylthiophosphate $(C_3H_7O)_2PSOC_6H_3Cl$-(2)-OC_2H_5-(4)	121-126	0.05	1.1883	1.5285	9.30, 9.30	8.79	19

water, and dried over sodium, or magnesium sulfates. The chlorobenzene was removed in vacuum, and the residue fractionated in vacuum.

The determination for phosphorous was conducted photocolorimetrically; sulfur, according to Carius.

SUMMARY

1. A series of dialkylalkoxyphenylthiophosphates and diethyl-4-thiocyanophenylthiophosphates, unreported in the literature, was synthesized in order to study their insecticidal properties.

2. A study of the insecticidal properties of the compounds obtained showed that they all were less active than diethyl-4-nitrophenylthiophosphate.

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* See Consultants Bureau Translation, page 441.

ter, and dried over sodium, or magnesium sulfate. The chlorobenzene was removed in vacuum, and the residue [illegible] [illegible] in vacuum.

The [illegible] of the compounds we [illegible] and [illegible] are given in Table.

SUMMARY

1. A series of dialkylamino-[illegible] and [illegible] [illegible], not described in the literature was synthesized in order to study their insecticidal properties.

2. A study of the insecticidal properties of the compounds obtained showed that they all were less active than diethyl-4-nitrophenylthiophosphate.

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* See Consultants Bureau Translation, page 393.

INVESTIGATION OF FURANE COMPOUNDS

IV. EXPERIMENTS ON THE ASYMMETRIC SYNTHESIS OF SPIRANES AND TETRAHYDROFURANE ALCOHOLS

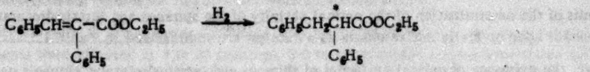
A. A. Ponomarev and V. V. Zelenkova

Among the recent investigations of asymmetric syntheses, those based upon the asymmetrizing action of optically active quartz crystals have attracted attention.

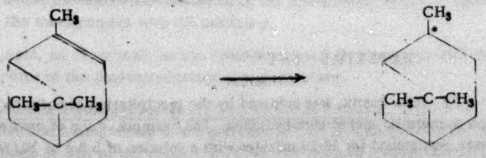
Ostromyslensky [1] first discovered the predominating separation of one of the optically active forms from a solution of the racemate under the influence of an optically active crystal of another organic substance. This was the start of further investigations on the asymmetrizing actions of crystals, in particular, asymmetric syntheses of various organic compounds with reactions conducted with the aid of catalysts deposited upon optically active quartz. Thus, Schwab and coworkers [2] conducted experiments upon the cleavage of secondary butyl alcohols with Cu, Ni, and Pt catalysts using an optically active form of quartz as the carrier. The undecomposed alcohol rotated the plane of polarization (α_D 0.1-0.13°) i.e., a preferential cleavage of one of the optically active forms occurred on the catalyst surface. Somewhat later Stankevich [3] repeated and widened the experiments of Schwab and attained an increase in the angle of rotation of the undecomposed alcohol to α_D 0.25°.

Both of the above investigations are examples of destructive asymmetric synthesis, i.e., the racemate is enriched by one optically active form because of the preferential decomposition of the second form.

The problem of asymmetric synthesis as a whole, and in particular of catalysis with the participation of a disymmetric crystalline lattice was subjected to a thorough theoretical and experimental examination in the investigations of A. P. Terentyev, E. I. Klabunovsky, and V. V. Patrikeev [4,5]. The above cited authors, in addition to further developing the destructive asymmetric synthesis, also successfully solved the problem of "synthetically absolute asymmetric synthesis". In particular, optically active forms of hydrogenated compounds were obtained by the hydrogenation of ethyl α-phenylcinnamate and α-pinene (optically inactive compounds) with a nickel catalyst deposited upon optically active quartz:

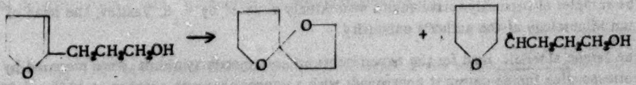


$$C_6H_5CH{=}\underset{\displaystyle C_6H_5}{\underset{|}{C}}-COOC_2H_5 \xrightarrow{H_2} C_6H_5CH_2\underset{\displaystyle C_6H_5}{\underset{|}{\overset{*}{C}}}HCOOC_2H_5$$

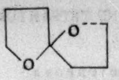


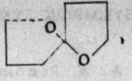
The maximum values of the rotation of the plane of polarization were +0.05° and − 0.09°, respectively. The hydrogenation experiments were conducted at usual pressure and 135° in decalin solution. The above investigation stimulated the idea of using a nickel quartz catalyst for the hydrogenation of furane alcohols.

As we know, spiranes are formed in addition to the corresponding tetrahydro alcohols by the catalytic hydrogenation of certain furane carbonyl compounds and alcohols. For example, 1,6-dioxaspiro-(4,4)-nonane and tetrahydrofurylpropanol are formed by the hydrogenation of furylpropanol.



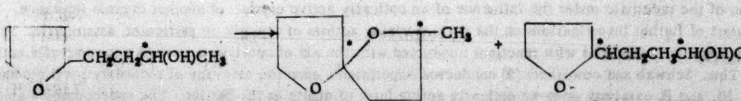
Homologs of dioxaspirononane were formed in an analogous manner by the hydrogenation of other γ-furylalkanols. The mechanism for the formation of the spiranes was discussed in the previous communication [10]. The stereochemistry of these bicyclic products has not been studied up to now, even though it is of undoubted interest especially in regard to the simplest of the spiranes of this type, 1,6-dioxaspirononane. Because of the presence of two hetero atoms and the mutually perpendicular distribution of the rings, the latter must exist in two optically active forms.





which is a very clear example of an optically active molecule not containing asymmetric carbon atoms.

The methyl homolog of this spirane arises by the hydrogenation of furylbutanol; tetrahydrofurylbutanol is formed at the same time:



Both of the products obtained already possess two asymmetric carbon atoms, and therefore, must each exist in the form of two racemates under the usual conditions.

In order to prove experimentally the optical activity of 1,6-dioxaspiro-(4,4) nonane, experiments on the asymmetric synthesis of this compound with a nickel quartz catalyst were conducted. In addition, the optical activity of the simultaneously obtained tetrahydrofurylpropanol, as well as that of the methyl homolog of the spirononane and tetrahydrofurane alcohol, obtained under analogous conditions, was proved by means of polarimetric measurement.

The hydrogenation experiments, in contrast to those of A. P. Terentyev, were conducted under pressures of 140-150 atm., which were necessary conditions for the formation of spiranes in satisfactory yields. Hydrogenation with simultaneous ring closure (for the formation of the spirane) also was a new type of reaction in comparison to the previous investigations on the asymmetric synthesis.

The results of the determination of the optical activity of the spiranes and tetrahydrofurane alcohols obtained by the use of nickel upon optically active quartz as a catalyst are summarized in Table 1.

Therefore, the existence of optical antipodes of spiranes and tetrahydrofurane alcohols can be considered experimentally proved.

EXPERIMENTAL

The catalyst, nickel on optically active quartz, was prepared by the precipitation of basic nickel carbonate on the quartz followed by reduction to metallic nickel with hydrogen. For example, 4.9 g of optically active quartz pulverized in an agate mortar, was ground for 15-20 minutes with a solution of 5.8 g of $Ni(NO_3)_2 \cdot 6H_2O$ in 8 ml of water. The homogenous mixture (homogeneity was kept by continuous efficient stirring) was added dropwise to a solution of 3.4 g of $(NH_4)_2CO_3$ in 20 ml of water. A thick mass with equally distributed particles of quartz and basic nickel carbonate was obtained. The precipitate was filtered, washed twice with small amounts of water, dried in a drying cabinet at 105-115°, and was carefully stored after being ground with glass rod. Weight of the catalyst obtained, 7.11 g. The ratio of the weight of the nickel carbonate to that of the carrier was 1:2.2. Directly before the hydrogenation, the catalyst was reduced with hydrogen at 300-320° until the formation of water stopped, and was cooled by a stream of CO_2.

The given procedure is usually applied for the preparation of nickel on kieselguhr [6].

The samples of optically active quartz were kindly donated by V. S. Vasilev, the head of the Chair of Petrography and Mineralogy of the author's university.

The furane alcohols used for the experiments on asymmetric synthesis were prepared by the hydrogenation of the corresponding furane carbonyl compounds with a copper-chromite catalyst at 120° and 90-120 atm of hydrogen pressure.

TABLE 1

Optical Activity of Several Hydrogenation Products of Furylpropanol and Furylbutanol Obtained with Nickel on Optically Active Quartz.

Starting substance	Hydrogenation products	Carrier	Tube length (in dm)	α°_D	Average error of determination F*
1-(α-Furyl)-propanol	1,6-Dioxaspiro-(4,4)-nonane	l-quartz	1.9	−0.066	±0.005
	1,6-Dioxaspiro-(4,4)-nonane	l-quartz	1	−0.03	±0.004
	1-Tetrahydrofurylpropanol-3	l-quartz	2	−0.04	±0.005
	1,6-Dioxaspiro-(4,4)-nonane	d-quartz	2	+0.06	±0.003
	1-Tetrahydrofurylpropanol-3	d-quartz	1.9	+0.04	±0.004
1-(α-Furyl)-butanol	2-Methyl-1,6-dioxaspiro-(4,4)-nonane	l-quartz	2	−0.02	±0.004
	1-Tetrahydrofurylbutanol-3	l-quartz	2	+0.03	±0.004
	2-Methyl-1,6-dioxaspiro-(4,4)-nonane	d-quartz	1.9	+0.02	±0.003
	1-Tetrahydrofurylbutanol-3	d-quartz	1.9	−0.04	±0.002

Furyl propanol was obtained from furylacrolein; it is an almost colorless liquid with b.p. 98-100° at 13mm, n^{20}_D 1.4752 (literature data: b.p. 98° at 10 mm, n^{25}_D 1.4760) [7]. 1-Furylbutanol-3 was obtained from furylacetone: it was a yellowish liquid with b.p. 126-129° at 52 mm, n^{21}_D 1.4748 (literature data: b.p. 126-128° at 55 mm, n^{25}_D 1.4744) [8].

The existence of optical activity for both furane alcohols was established by polarimetric measurement.

Experiments on asymmetric synthesis with nickel quartz catalyst were conducted at 120° and an initial pressure of 135-150 atm of hydrogen in absolute alcohol solution. Upon exhaustive hydrogenation under these conditions, 1-1.3 moles of hydrogen were absorbed per mole of alcohol used for the experiment. At the end of hydrogenation, the catalyst was filtered, and the hydrogenizate (after removal of the alcohol) was subjected to vacuum distillation. By redistillation, narrow fractions were isolated which corresponded to the spiranes and tetrahydrofurane alcohols in boiling point and refractive indices (Table 2).

The total yield of the spirane and tetrahydrofurane alcohol was 71.5% for furylpropanol with l-quartz, 48.2% with d-quartz; the corresponding figures for furylbutanol were 87.4% and 85.2%.

Measurement of the optical activity was conducted with a Lippikh polarimeter (Firm of Schmidt and Gench). All of the measurements were effected at 6 to 25 readings; 2-3 series of measurements were made with the same substance. The determination of the zero point of the polarimeter, as a rule, was conducted with an empty tube before and after the measurement with the substance.

As an example, an experiment on the hydrogenation of furylpropanol with nickel on d-quartz, and the polarimetric measurements of the products obtained, are given below.

Hydrogenation of 1-(α-furyl)-propanol with nickel on d-quartz. 70 g of furylpropanol was dissolved in 80 ml of absolute alcohol and hydrogenated in the presence of 15.5 g of nickel on d-quartz (ratio of weight of the nickel carbonate precipitate to that of the carrier, 1:12) at 120° with an initial pressure of 142 atm of hydrogen. 14 liters of hydrogen were absorbed within 4 hours, i.e., 1.2 moles of hydrogen per mole of alcohol. The catalyst was filtered, the alcohol removed, and the residue subjected to vacuum distillation. The distillate was separated into two fractions by redistillation.

I. Dioxaspirononane, b.p. 81-82° at 60 mm, n^{20}_D 1.4478, weight 13.03 g (18.6%). II. Tetrahydrofurylpropanol, b.p. 141-144° at 60 mm, n^{20}_D 1.4592, weight 21.07 g (29.6%).

The fractions were used for the measurement of the optical activity of both products (Tables 3 and 4).

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*The average error of determination F was calculated according to the formula:

$$F = \sqrt{\frac{\Sigma (f_m^2)}{n(n-1)}}$$ where $f_m = m - M$ is the difference between the value of the rotation of the given and the arithmetic average, n is the number of measurements.

TABLE 2

Several Constants of Spiranes and Tetrahydrofurane Alcohols Obtained as Results of Experiments on Asymmetric Synthesis

Name of substance	Boiling point (in °)	n_D^{25}	Literature data [9]	
			b.p. (in °)	n_D^{25}
1,6-Dioxaspiro-(4,4)-nonane	83-84 (62 mm) 81-82 (60 mm)	1,4464 1,4465	81-82 (60 mm)	1.4465
1-(α-Tetrahydrofuryl) propanol-3	139-144 (58 mm) 141-144 (60 mm)	1,4595 1,4580	144 (60 mm)	1,4563
2-Methyl-1,6-dioxaspiro-(4,4)-nonane	77-73 (43 mm) 79-81 (46 mm)	1,4410 1,4415	80 (46 mm)	1,4412
1-(α-Tetrahydrofuryl)-butanol-3	128-130 (44 mm) 131-133 (48 mm)	1,4570 1,4542	145 (58 mm)	1,4541

TABLE 3

Measurement of the Optical Activity of 1,6-Dioxaspiro-(4,4)-nonane Obtained by the Hydrogenation of Furylpropanol with Nickel on d-Quartz.

Zero point with 2 dm tube	Measurement with tube filled with the spirane	Zero point of the tube after measurement
0.19	0.25	0.20
0.18	0.25	0.20
0.18	0.26	0.21
0.20	0.25	0.19
0.17	0.25	0.20
0.16	0.25	0.20
0.19	0.24	0.22
0.17	0.26	0.21
0.17	0.24	0.22
0.20	0.26	0.20
0.16	0.26	–
0.16	0.26	–
0.18	–	–
0.17	–	–
0.18	–	–
Average of 15 readings 0.177° F ± 0.003°	Average of 12 readings 0.251° F ± 0.002°	Average of 10 readings 0.205° F ± 0.003°

Average zero point 0.191°; $\alpha_D^{21.5}$ + 0.06°

TABLE 4

Measurement of the Optical Activity of 1-(α-Tetrahydrofuryl)-propanol-3 Obtained by the Hydrogenation of Furylpropanol with Nickel on d-Quartz.

Zero point with 2 dm tube	Measurement with tube filled with tetrahydrofuryl propanol	Zero point of the tube after measurement
0.23	0.25	0.21
0.23	0.24	0.24
0.23	0.28	0.24
0.23	0.26	0.23
0.24	0.26	0.23
0.22	0.25	0.24
0.21	0.26	0.22
0.21	0.26	0.23
0.23	0.26	0.21
0.23	0.26	0.23
0.22	–	–
0.22	–	–
0.22	–	–
0.21	–	–
0.24	–	–
Average of 15 readings 0.224 F ± 0.002°	Average of 10 readings 0.268° F ± 0.004°	Average of 10 readings 0.228° F ± 0.004°

Average zero point 0.226°; α_D^{19} + 0.042°

SUMMARY

1. An asymmetric synthesis of 1,6-dioxaspirononane was accomplished which proved, experimentally, the theoretical belief of the stereoisomerism of this compound.

2. The fact of asymmetric synthesis with a nickel catalyst deposited on l- and d-quartz was established, which was also accompanied by the intramolecular cyclization (formation of spiranes).

At the same time, the practical possibility to realize an asymmetric synthesis in the presence of the above catalyst at high pressures and temperature was shown on the example of the hydrogenation of furylpropanol and furylbutanol.

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SYNTHESIS
OF AROMATIC ORGANOELEMENTAL COMPOUNDS
BY THE REACTION OF ARYL SILANES WITH ALUMINUM CHLORIDE
AND HALIDES OF VARIOUS ELEMENTS

I. ORGANOPHOSPHOROUS COMPOUNDS

A. Ya. Yakubovich and G. V. Motsarev

Several methods are known for the preparation of alryldichlorophosphines. Thus, they can be prepared by passing vapors of aromatic hydrocarbons with phosphorus trichloride through an incandescent porcelain or glass tube [1]. Another method for the preparation of these compounds is based upon the use of organo mercury compounds. For example, $C_6H_5PCl_2$ can be obtained by the reaction between $(C_6H_5)_2Hg$ and PCl_3 [2].

The most satisfactory of all of the known methods of synthesis of aryl dichlorophosphines is their preparation by the reaction of aromatic halogen derivatives (benzene, chloro- and bromobenzene, toluene, xylene, and others) with phosphorus trichloride in the presence of anhydrous aluminum chloride as a catalyst [3-7]. Nevertheless, this method is not free of shortcomings, the main one of which is the formation of several isomers during the reaction.

Therefore, the known methods for the preparation of aryl dichlorophosphines show that these compounds are still relatively poorly available substances, without even considering their derivatives containing various substituents in the aromatic radical.

Because the authors previously showed that dichlorophosphines were formed by the action of PCl_3 upon the product of the reaction between phenyl trichlorosilane and anhydrous $AlCl_3$ [8], a detailed investigation of this reaction was undertaken in order to determine the possibility and the conditions for the synthesis of various aromatic organo phosphorus compounds by this method. The present communication reports on the results of the investigation on the synthesis of aromatic dichlorophosphines and their derivatives with various substituents in the aromatic ring.

The method reported below for the preparation of aryl dichlorophosphines and their derivatives is based on the use of aromatic silanes of the general formula $(C_6H_{5-n}X_n)_mSiCl_{4-m}$ (where m = from 1 to 4) which are reacted with phosphorus trichloride in the presence of anhydrous aluminum chloride.

The formation of aromatic organo phosphorus compounds with this reaction occurs because the aromatic silanes and their derivatives (with substituents in the aromatic ring), as was previously shown by the authors in one of the previous communications [8], undergo a cleavage of the C − Si bond under the influence of aluminum chloride with the formation of the corresponding organo-aluminum compounds of the type $ArAlCl_2$. Such compounds react with PCl_3 as a result of which the corresponding aromatic aryl dichlorophosphines are obtained.

This course of the reaction may be represented in a general form by the following series of equations:

$$(C_6H_{5-n}X_n)_mSiCl_{4-m} + mAlCl_3 \rightarrow mC_6H_{5-n}X_nAlCl_2 + SiCl_4$$

$$mC_6H_{5-n}X_nAlCl_2 + mPCl_3 \rightarrow mC_6H_{5-n}X_nPCl_2 + mAlCl_3$$

Where X = H, Cl, Br, I, R, etc., m = From 1 to 4, n = From 0 to 5

The phosphorus trichloride can enter into reaction in two ways: either simultaneously with the aromatic silane and aluminum chloride, which leads to the reaction of PCl_3 with the organo-aluminum compound at the moment of its formation; or after the aromatic silane is decomposed by the aluminum chloride, followed by the removal of the silicon tetrachloride from the reaction mass. In a preparative relation the first course is more convenient without even considering that it leads to the preparation of aryl dichlorophosphines with somewhat higher yields.

In order to prepare aryl dichlorophosphines by this method, the aromatic silane, for example an aryl trichlorosilane, is mixed with phosphorus trichloride and aluminum chloride in a ratio of $ArSiCl_3 : PCl_3 : AlCl_3 = 1.0 : 1.0 : 1.1$. Even the simple mixing of the mixture of the above reagents leads to the heating up of the mixture and a gradual solution of the aluminum chloride. With further heating of the reaction mixture to 80°, an almost complete solution of the aluminum chloride and the separation of the reaction mixture into two layers occurs; the upper one, colorless, is silicon tetrachloride, and the lower one, oily light brown. The latter is the complex compound of aryl dichlorophosphine with aluminum chloride.

If phosphorus oxychloride acts upon this complex after the removal of the silicon tetrachloride, the aryl dichlorophosphine is displaced from it, and a new complex $POCl_3 \cdot AlCl_3$ is formed which makes the isolation of the aryl dichlorophosphine in pure form possible. In this manner, phenyl-, p-chlorophenyl, p-bromophenyl, and p-tolylphenyldichlorophosphines were isolated in good yields.

The above examples show that the method reported above can serve as a convenient general method for the synthesis of primary dichlorophosphines and their various derivatives.

With the aid of the organo aluminum compounds, formed as intermediate products by the reaction of phenylchlorosilanes with $AlCl_3$, not only can the aryl dichlorophosphines be prepared, but also the acid chlorides of the aryl phosphinic acids. This reaction was studied by means of the reaction of phenyltrichlorosilane with $AlCl_3$ and phosphorus pentachloride. The formation of phenylphosphenyl chloride occurs in this case according to the scheme:

$$C_6H_5SiCl_3 + AlCl_3 \rightarrow C_6H_5AlCl_2 + SiCl_4 \quad C_6H_5AlCl_2 + PCl_5 \rightarrow C_6H_5PCl_4 + AlCl_3 \rightarrow C_6H_5PCl_4 \cdot AlCl_3,$$

$$C_6H_5PCl_4 \cdot AlCl_3 + POCl_3 \rightarrow C_6H_5PCl_4 + AlCl_3 \cdot POCl_3, \quad C_6H_5PCl_4 + SO_2 \xrightarrow{\text{(in } CCl_4 \text{ solution)}} C_6H_5POCl_2 + SOCl_2.$$

It is interesting to mention that phosphorus oxychloride in contrast to phosphorus pentachloride, does not react with phenyl aluminum dichloride.

EXPERIMENTAL

I. Phenyl Dichlorophosphine $C_6H_5PCl_2$

1. Preparation from $C_6H_5SiCl_3$. a) PCl_3 was introduced into the reaction simultaneously with the $C_6H_5SiCl_3$ and $AlCl_3$. 100.0 g of phenyltrichlorsilane, 69.3 g of freshly sublimed anhydrous aluminum chloride, and 65.0 g of phosphorus trichloride were placed into a round-bottomed flask connected to a condenser and a trap cooled with an acetone carbon dioxide mixture (−40°), and fitted with a calcium chloride tube. The mixture was heated for 2 hours on the water bath at 80°, and then the silicon tetrachloride was removed (by shutting off the reflux condenser and putting on the vacuum). 75.5 g of silicon tetrachloride (yield 94.4% of the theoretical) was obtained in the receiver 85.8 g of phosphorus oxychloride was added gradually to the hot oil-like residue in the flask after the removal of the $SiCl_4$ which led to the formation of a grainy precipitate. The precipitate was treated with several portions of petroleum ether, the extracts were combined, the petroleum ether was removed, and the residue vacuum distilled Vacuum distillation resulted in 70.0 g (83.4%) of phenyldichlorophosphine in the form of a strongly refractive, light yellow liquid with a b.p. of 140-141° (57 mm), d_{20}^{20} 1.3180, which fumed in the air and possessed a sharp unpleasant odor (literature data: b.p. 222, 140-142° (57 mm) d^{20} 1.319 [2]).

0.2083, 0.2004 g substance. In 25 ml 0.5 N KOH: 22.9, 21.95 ml 0.1 N $AgNO_3$. Found%: hydrolyzable Cl 39.02, 38.94. $C_6H_5PCl_2$. Calculated %: Cl 39.66.

b) PCl_3 was introduced into the reaction after the cleavage of $C_6H_5SiCl_3$ by aluminum chloride and after the removal of $SiCl_4$. 20.0 g of phenyltrichlorosilane and 13.9 g of freshly sublimed anhydrous aluminum chloride were placed into a round-bottomed flask fitted to a calcium chloride tube and connected in the same manner as in the previous experiment, with a reflux condenser and a receiver. Upon mixing the reagents, the reaction mass turned red. In order to accelerate the reaction, the mixture was heated at 70-80°, with the simultaneous removal of the silicon tetrachloride formed, by connecting the entire system to a vacuum.

13.9 g of $SiCl_4$ or 87.0% were obtained in the receiver. 13.0 g of phosphorus trichloride was added gradually to the semi-solid brown residue after the removal of the $SiCl_4$. After the addition of all of the PCl_3, the mixture became liquid. The mixture was heated for 1 hour at 80-90°, and then 17.2 g of phosphorus oxychloride was added gradually to it. The further isolation of phenyldichlorosilane was conducted in analogous manner to that reported above. 12.8 g of phenyldichlorophosphine with b.p. 140° (56 mm) was obtained. Yield, 76.0% of the theoretical based upon the starting phenyltrichlorosilane.

0.2321, 0.1972 g substance in 25 ml 0.5 N KOH: 25.6, 21.55 ml 0.1 N $AgNO_3$. Found %: Hydrolyzable Cl. 39.14, 38.83. $C_6H_5PCl_2$. Calculated %: Cl 39.66.

2. Preparation from $(C_6H_5)_2SiCl_2$. A mixture consisting of 10.0 g diphenyldichlorosilane, 11.6 g of freshly sublimed aluminum chloride, and 11.0 g of phosphorus trichloride was heated for 3 hours on the water bath at 80°. Silicon tetrachloride was distilled from the reaction mass which had separated into layers (6.2 g or 92.7% of the theoretical), and 14.3 g of phosphorus oxychloride was slowly added to the residue. The phenyldichlorophosphine was then isolated by the above reported method. 11.3 g of phenyldichlorophosphine with b.p. 138-139° (55 mm) was obtained. (Yield, 80.4% of the theoretical).

0.1826, 0.2233 g substance in 25 ml 0.5 N KOH: 20.0, 24.6 ml 0.1 N $AgNO_3$. Found %: Hydrolyzable Cl. 38.91, 39.10. $C_6H_5PCl_2$. Calculated %: Cl 39.66.

II. p-Chlorophenyldichlorophosphine p-$ClC_6H_4PCl_2$.

10.0 g of p-chlorophenyltrichlorosilane, obtained, either as the result of the reaction of p-ClC_6H_4MgBr with $SiCl_4$ [9], or by the chlorination of phenyltrichlorosilane in the presence of a catalyst [10], was mixed with 6.0 g of freshly sublimed aluminum chloride, and 5.7 g of phosphorus trichloride. The mixture was heated for 2 hours on the water bath at 80°; the silicon tetrachloride was then removed (6.3 g or 90.7%), 7.0 g of phosphorus oxychloride was gradually added to the results.

The isolation of p-chlorophenyldichlorophosphine was effected by a method analogous to that reported for the isolation of phenyldichlorophosphine. 6.6 g of p-chlorophenyldichlorophosphine was obtained in the form of a colorless oil-like liquid with an unpleasant odor and b.p. of 252-253°, d_{20}^{20} 1.4203. (Literature data: b.p. 253-255°, d^{17} 1.425 [5]). Yield, 77.4% of the theoretical based on p-chlorophenyltrichlorosilane.

0.2381, 0.2452 g substance in 25 ml 0.5 N KOH: 21.9, 22.6 ml 0.1 N $AgNO_3$. 0.1420, 0.1137 g substance; 0.2823, 0.2255 g AgCl (Carius). Found %: Hydrolyzable Cl 32.67, 32.74; Total Cl 49.21, 49.09. $ClC_6H_4PCl_2$. Calculated %: Hydrolyzable Cl 33.25; Total Cl 49.88.

III. p-Bromophenyldichlorophosphine p-$BrC_6H_4PCl_2$.

10.0 g of p-bromophenyltrichlorosilane, obtained either by means of the organo magnesium synthesis by the reaction of p-BrC_6H_4MgBr with $SiCl_4$ [9], or by the bromination of phenyltrichlorosilane in the presence of a catalyst [11], was mixed with 5.0 g of freshly sublimed aluminum chloride and 4.7 g of phosphorus trichloride. The mixture was heated for 2 hours on the water bath at 80°; the silicon tetrachloride was then removed (5.2 g or 89.6%), and 5.9 g of phosphorus oxychloride was added gradually to the residue. The isolation of p-bromophenyldichlorophosphine was effected by the same method (see the previous experiment). 6.4 g of p-bromophenyldichlorophosphine was obtained in the form of a colorless, highly refractive, thick liquid with a b.p. of 270°, d_{20}^{20} 1.6861. (literature data: 271-272°, d^{15} 1.6895 [5]). Yield 72.6%, based on the p-bromophenyltrichlorosilane used for the reaction.

0.2520, 0.2310 g substance in 25 ml 0.5 N. KOH: 19.1, 17.6 ml 0.1 N $AgNO_3$. Found %: Hydrolyzable Cl 26.91, 27.03. $BrC_6H_4PCl_2$. Calculated %: Hydrolyzable Cl 27.51.

Upon treatment with water, p-bromophenylphosphinic acid was obtained which was analyzed for bromine content. 3 g of p-bromophenyldichlorophosphine was dropped into 10 ml of water. The precipitate which formed, was filtered and washed with cold water (3-5°). After recrystallizing it from aqueous alcohol, thin platelets with m.p. 142.3° were obtained, which corresponded to the melting point of p-bromophenylphosphinic acid (literature data: m.p. 143° [5]).

0.1276, 0.1451 g substance; 0.1067, 0.1220 g AgBr (Carius). Found %: Br 35.61, 35.82. $BrC_6H_4P(OH)_2$. Calculated %: Br 36.19.

IV. p-Tolyldichlorophosphine p-$CH_3C_6H_4PCl_2$.

10.0 g p-tolyldichlorosilane, synthesized from p-$CH_3C_6H_4MgBr$ and $SiCl_4$, was mixed with 6.5 g of freshly sublimed aluminum chloride and 6.1 g of phosphorus trichloride. The mixture was heated on the water bath for 2 hours at 80°; the silicon tetrachloride was then removed (7.0 g or 93.8%), and 7.5 g of phosphorus oxychloride was gradually added to the residue.

The subsequent isolation of p-tolyldichlorophosphine from the reaction mass was accomplished by the method reported above for other phosphines. 7.2 g of p-tolyldichlorophosphine (85.3%) was obtained in the form of a colorless, crystalline substance (platelets from ether) with m.p. 24.5°, b.p. 243-244° (literature b.p. 245°, m.p. 25° [4]).

0.2119, 0.2334 g substance in 25 ml 0.5 N KOH: 21.55, 23.65 ml 0.1 N $AgNO_3$. Found %: Hydrolyzable Cl. 36.11, 36.01. $CH_3C_6H_4PCl_2$. Calculated %: Hydrolyzable Cl 36.78.

V. Reaction of Phenyltrichlorosilane with $AlCl_3$ and PCl_5. Preparation of Phenylphosphenyl chloride $C_6H_5POCl_2$. 40.0 g of phenyltrichlorosilane was added with stirring to a mixture of 30.2 g of freshly sublimed aluminum chloride and 39.4 g of phosphorous pentachloride. Upon the addition of phenyltrichlorosilane, a noticeable evolution of heat occurred, and the reaction mass became red brown. Heating of the mixture for 2 hours at 80-85° led to almost complete disappearance of the solid phase and the formation of two layers: the upper layer was very mobile and colorless; the lower, brown, oil-like. In order to remove the silicon tetrachloride, the reaction mass was heated on the water bath in vacuum.

28.7 g of $SiCl_4$ (yield 89.6% of the theoretical) was obtained in the receiver cooled with acetone-carbon dioxide mixture (−40°). 38.2 g of phosphorus oxychloride was added to the cooled residue obtained after the removal of the silicon tetrachloride, which led to the formation of a precipitate. After the addition of all of the $POCl_3$, the reaction mass was heated for 1 hour at 70°, 40.0 ml of carbon tetrachloride was added to it, and it was treated in the cold with dry sulfur dioxide until the evolution of heat stopped. The liquid part was separated from the solid grainy residue and subjected to fractionation. The main part of the CCl_4 in a mixture with $SOCl_2$ was distilled at atmospheric pressure, and the remainder and the $POCl_3$ was removed in vacuum. The residue after the removal of the solvents, was distilled from a metallic bath at usual pressure. The following fractions were collected: 1 with b.p. 193-199°−4.0 g, 2 with b.p. 200-250°−0.8 g, 3 with b.p. 250-259°−19.6 g. Fraction 1 was redistilled at ordinary pressure; 3.5 g of a liquid with b.p. 197-199° was obtained; it was phenyltrichlorosilane.

0.2374, 0.2462 g substance. in 25 ml 0.5 N alcoholic KOH: 33.2, 34.5 ml 0.1 N $AgNO_3$. Found %: Hydrolyzable Cl 49.7, 49.8. $C_6H_5SiCl_3$. Calculated %: Hydrolyzable Cl 50.3.

Fraction 3 was redistilled at ordinary pressure. 16.8 g of a liquid with b.p. 256-258° and d_{20}^{20} 1.3700. Yield 45.6% of the theoretical.

0.2167, 0.2226 g substance in 25 ml 0.5 N KOH: 21.85, 22.55 ml 0.1 N $AgNO_3$. Found %: Hydrolyzable Cl. 35.84, 35.97. $C_6H_5POCl_2$. Calculated %: Hydrolyzable Cl 36.41.

Therefore, fraction 3 was phenylphosphenyl chloride the constants of which were reported by Michaelis [2]: b.p. 258°, d^{20} 1.375.

VI. Reaction of Phenyltrichlorosilane with $AlCl_3$ and $POCl_3$

A mixture of 30.0 g of phenyltrichlorosilane and 20.7 g of freshly sublimed aluminum chloride was heated for 4 hours on the water bath at 80°. Toward the end of the heating, the reaction mixture acquired a red brown color and boiled violently. After cooling to 30°, 68.7 g of phosphorus oxychloride was added to it; the addition was accompanied by a noticeable heating up of the reaction mixture. At the end of the addition of the $POCl_3$, the reaction mixture was heated for 1 hour at 80°, and the volatile products were removed from it in vacuum. About 50.0 g of a liquid was obtained in the receiver cooled with acetone carbon dioxide mixture (−40°), which yielded the following fractions upon distillation: 1 with b.p. 54-60°−14.2 g, 2 with b.p. 60-102°−2.6 g, 3 with b.p. 102-108°− 31.2 g.

Fraction 1 represented silicon tetrachloride, with b.p. 56-57°, d_{20}^{20} 1.4820.

Fraction 3 was redistilled at ordinary pressure. The main part distilled at 105-107°.

Found %: Cl 68.71, 69.02. $POCl_3$. Calculated %: Cl 69.38.

Therefore, fraction 3 was phosphorus oxychloride.

The semi-solid residue, obtained after the distillation of the volatile products, was treated with several portions of petroleum ether, the extracts combined, the ether removed, and the residue distilled first at atmospheric pressure, and then in vacuum.

Upon distillation, 5.0 g of phosphorus oxychloride (b.p. 103-108°) and 10.0 g of a fraction with b.p. 196-199° (70-72° at 7 mm), which was unchanged phenyltrichlorosilane, were obtained. The residue after the distillation had the form of thick oil-like liquid, which violently decomposed in water.

In another experiment, the treatment of the semi-solid residue after the removal of the volatile products, was with benzene instead of petroleum ether; however, the same results were obtained as in the previous experiment.

SUMMARY

1. Primary aryl chlorophosphines were formed in good yields by the reaction of phosphorous trichloride with an organoaluminum compound obtained by the reaction of aryl chlorosilanes with $AlCl_3$. Aryl dichlorosilanes containing substituents such as Cl, Br, CH_3 in the ring can also be obtained in this manner.

2. Phosphorus pentachloride reacted with phenyltrichlorosilane and $AlCl_3$ to form phenyltetrachlorophosphine which was readily converted to phenylphosphenyl chloride. In contrast to PCl_5, phosphorus oxychloride did not give compounds with a C—P bond with an analogous reaction.

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* See Consultants Bureau Translation, page 1111.

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distillation had the form of thick oil-like liquid, which violently decomposed in water.

In another experiment, the treatment of the semi-liquid residue after the distillation of the volatile products, with benzene instead of petroleum ether; however, the same results were obtained as in the previous experiment.

SUMMARY

1. Primary aryl chlorophosphines were formed in good yields by the reaction of phosphorus trichloride with organomercury compounds obtained by the reaction of aryl derivatives with $AlCl_3$. Aryl dichlorophosphines containing substituents such as Cl, Br, C_2H_5 [illegible] were obtained in this manner.

2. Phosphorus pentachloride reacted with ethylene, benzene and $AlCl_3$ to form phosphorus chloride complexes which were readily converted to phenyl phosphonyl chloride. In contrast to PCl_5, thiophosphoryl chloride did not give compounds with a C-P bond with an analogous reaction.

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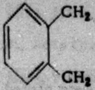
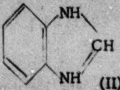
NITRATION OF PIAZTHIOL

L. S. Efros and R. M. Levit

Generalizing the literature data upon the appearance of disruption of equalization of bonds in benzene rings entering into the composition of molecules with condensed nuclei, it can be concluded that three types of this phenomena are conceivable and exist in practice, depending on the degree of affinity of the adjacent ring to π-electrons.

In the first case, the adjacent ring repels π-electrons of the benzene ring from itself, and decreases the π-electron density of bonds common for both rings. Hydrindin (I) can serve as an example of a compound of this type [1]. In the second case, the adjacent ring possesses approximately the same affinity to the electrons as the benzene ring; characteristic compounds of this type are naphthalene, and as the authors showed [2] benzimidazole (II). Finally, in the case where the adjacent ring possesses a noticeably greater affinity for the electrons than benzene, there is a third type of disruption of the equalization of the bonds; piazthiol is a graphic example of such a compound; measurement of the interatomic distance of which [3] shows that it has the structure (III).


(I)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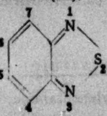

(III)

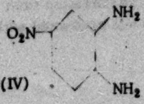
The disruption of equalization of the bonds in the benzene ring of imidazole, shown in formula (II) was found by studying the chemical properties of this compound [2]. On the other hand, a series of generalities in chemical behavior of substances with imidazole rings could be predicted using this representation of the phenomenon [4, 5].

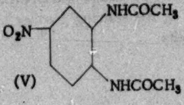
It seemed of interest to proceed in another manner in the case of piazthiol, and to predict certain chemical properties of this substance, knowing its fine structure on the basis of the measurement of the interatomic distances. Thus, it was clear that in contrast to benzimidazole (II), the nitrogen atom in piazthiol (III) must cause a partial positive charge in positions 5 and 6, because of which the nitration of this compound should lead to the entrance of the substituent predominantly into positions 4 and 7.

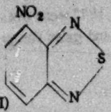
Meanwhile, A. M. Khaletsky and V. G. Pesin [6], in a recently-published paper on the study of the nitration of piazthiol, stated that the product obtained by them was a 5-nitro derivative. They proved this structure by synthesizing this product from 4-nitro-1,2-phenylenediamine (IV) and thionyl chloride. Diamine (IV) they obtained by the acid hydrolysis of 4-nitro-1,2-diacetyldiaminobenzene (V).

Since it is known that, mainly, cyclization with the formation of 5-nitro-2-methylbenzimidazole occurs upon acid hydrolysis of compound (V) [7], and only traces of diamine (IV) are obtained, and since the conclusions on the structure of nitropiazthiol are based on these experiments and are in opposition to the conclusions from the above-theoretical views, it was decided to clarify this problem.

4-Nitro-1,2-phenylene diamine (IV) and 3-nitro-1,2-phenylenediamine, isomeric with it, were obtained in chemically pure form by known methods, partial reduction of 2,4-dinitroaniline and 2,6-dinitroaniline which was obtained by the authors. Upon treating 3-nitro-1,2-phenylenediamine with thionyl chloride under conditions reported by A. M. Khaletsky and V. G. Pesin, 4-nitropiazthiol (VI) was obtained which was identical with the nitration product of piazthiol:

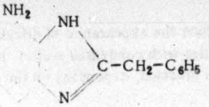

(IV)


(V)


(VI)

It is interesting that 4-nitrophenylenediamine (IV) only reacts weekly with thionyl chloride in an analogous manner, which is readily explained by the electrophyllic effect of the nitro group, which hinders the closing of the piazthiol ring.

For the final proof of the structure of the nitration product of piazthiol, this product was reduced with zinc and hydrochloric acid. The piazthiol ring was completely destroyed, and consecutive triaminobenzene hydrochloride was isolated from the reaction mass with a good yield The previously reported [5] 4-amino-2-benzylbenzimidazole (VII) was obtained from it by condensation with phenylacetic acid:



(VII)

Both of these products were identified against those obtained by the usual methods reported in the literature.

Therefore, the theoretical prognosis on the direction of the nitration of piazthiol, which was derived from a representation of the disruption of the equality of the bonds in its benzene ring, was completely proved.

The nitration of piazthiol followed by reduction of this compound occurring with the disruption of the heterocycle can be recommended as a method for the preparation of consecutive triaminobenzene since this product is synthesized with comparative difficulty by methods reported in the literature.

EXPERIMENTAL

Preparation of Piazthiol

50 g of o-phenylenediamine, 800 ml of toluene, and 150 g of thionyl chloride were placed in a flask equipped with a reflux condenser and calcium chloride tube. The mixture was heated for 12 hours on an oil bath. The toluene was then distilled from the flask by means of a herringbone dephlegmator, and the crude reaction product was subjected to vacuum distillation for final purification. Piazthiol distilled at 79-80° at 5 mm. 54.5 (86.5 %), of piazthiol was obtained in the form of a crystalline substance melting at 42-44°.

Preparation of 4-nitropiazthiol (According to Khaletsky and Pesin's method)

20 g of piazthiol and 56 ml of concentrated sulfuric acid (d 1.84) were placed into a flask equipped with a stirrer. A nitration mixture consisting of 12 ml of nitric acid (d 1.4) and 18 ml of concentrated sulfuric acid was added slowly from a dropping funnel. The nitration was conducted at 0°. At the end of the nitration, the reaction mixture was kept 0.5 hours at room temperature, and then poured on ice. A light yellow precipitate formed which was filtered and washed with cold water to a neutral reaction. The light yellow substance obtained after recrystallization from alcohol, melted at 107°. 25.5 g of nitropiazthiol (90.5%) was obtained.

Preparation of 4-Nitropiazthiol from 1-Nitro-2,3-diaminobenzene.

1 g of 1-nitro-2,3-diaminobenzene with m.p. 156° obtained in the usual manner from 2,6-dinitroaniline, 30 ml of absolute dry toluene, and 2 g of thionyl chloride were placed in a flask equipped with a reflux condenser and a calcium chloride tube. The mixture was heated for 6 hours on an oil bath, filtered and poured into a crystallizer. 0.8 g of a light yellow substance (67.8%) with m.p. 107-108° was obtained upon recrystallization from water.

Attempts to prepare 5-Nitropiazthiol from 1-Nitro-3,4-diaminobenzene

2 g of 1-nitro-3,4-diaminobenzene, m.p. 197-198° obtained in the usual manner from 2,4-dinitroaniline, 40 ml absolute dry toluene, and 4 g of thionyl chloride were placed into a flask equipped with a reflux condenser and a calcium chloride tube. The mixture was heated for 6 hours, filtered, and poured into a crystallizer. Upon evaporation of the toluene, a brown crystalline substance was obtained. After recrystallization from toluene, dark red crystals with m.p. 197° were obtained, i.e., the starting product. The synthesis was conducted with a double quantity of thionyl chloride and gave the same results.

Preparation of 1,2,3-Triaminobenzene from 4-Nitropiazthiol

2.4 g of 4-nitropiazthiol was dissolved in 100 ml of hot water with 30 ml of concentrated hydrochloric acid. 12 g of zinc dust was added to the solution as rapidly as possible; a reduction occurred with a violent evolution of hydrogen sulfide. The solution obtained was filtered from impurities, 1,2,3-triaminobenzene dihydrochloride was obtained by the addition of 25 ml of concentrated hydrochloric acid in the form of long, thin needles. The salt was separated, dissolved in 20 ml of water, and the solution was shaken in the cold with activated carbon, filtered and colorless needles of the same salt of triaminobenzene were formed by the addition of concentrated hydrochloric acid. Yield, 1.8 g which was 67% of the theoretical amount

Upon condensation with phenylacetic acid [5], 4-amino-2-benzylbenzimidazole (VII) was obtained, whose salt melted at 242-248°, the base at 154°.

SUMMARY

1. The 4-nitro derivative was formed upon the nitration of piazthiol in complete agreement with developed theoretical principles and in contrast to the literature data.

2. The nitration of piazthiol, followed by the reduction of the product which occurred with the disruption of the heterocycle, is a convenient method for the synthesis of vicinal triaminobenzene.

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* See Consultants Bureau English Translation, page 1003.
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**** See Consultants Bureau English Translation, page 1981.

[illegible]

2.4 g of [illegible] was dissolved in [illegible] 12 g of zinc dust was added to the solution [illegible] hydrogen chloride. The solution obtained [illegible] obtained by the addition of 30 ml of concentrated [illegible] was separated, dissolved in 30 ml of water, and the [illegible] and colorless needles of the same [illegible] Yield, 1.8 g which was 87% of the theoretical amount.

Upon condensation with [illegible] acid [illegible] melting point is [illegible] the same as [illegible].

SUMMARY

1. The [illegible]

2. [illegible]

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[illegible] Organic Dyes [illegible]
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* See Consultants Bureau English Translation, page [illegible]

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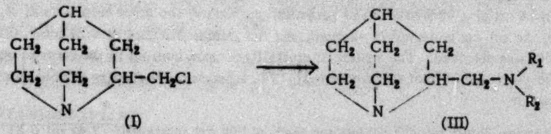
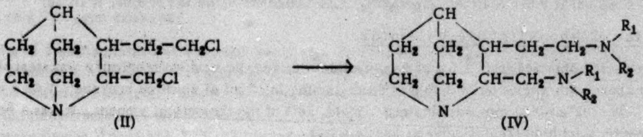
ALKYLAMINO DERIVATIVES OF QUINUCLIDINE

M. V. Rubtsov, E. S. Nikitskaya, E. E. Mikhlina,
A. D. Yanina, and V. Ya. Furshtatova

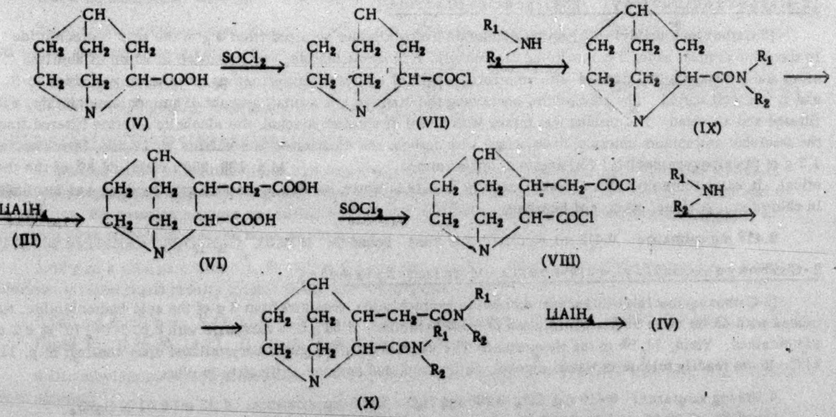
Attempts to obtain alkylamino derivatives of quinuclidine from the previous reported chloroderivatives (I and II) [1, 2] were unsuccessful because of the small activity of the chlorine found in the chloromethyl group of the quinuclidine ring.


(I) (III)


(II) (IV)

The synthesis of compounds (III) and (IV) was effected by the reduction of the corresponding amides with lithium aluminum hydride.

The reactions for the preparation of the amides and their reduction into the corresponding amines can be expressed by the following schemes:


(V) (VII) (IX) (VI) (VIII) (X)

2-Quinuclidine carboxylic acid (V) and [2-carboxyquinuclidyl-(3)]-acetic acid (VI) were converted into the acid chlorides (VII and VIII) by means of thionyl chloride. These were treated with ammonia or alkyl (aryl) amines, which resulted in the formation of the corresponding amides (IX and X). Compounds (III) and (IV) were obtained by the reduction of the amides with lithium aluminum hydride.

The yield of the amine depends on the solubility of the starting amide in ether, or benzene in which the reduction reaction was conducted With sufficiently good solubility of the amide in the above solvents, the amines are obtained with yields of 70-80%. Poor solubility of the amide leads to a sharp decrease of the yield. Thus, 2-quinuclidine carboxamide [3], difficultly soluble in ether and insoluble in benzene, is reduced with a yield of about 40% of the amine, [2-carboxyquinuclidyl -(3)]-acetic diamide. practically insoluble in ether and benzene, does not react with lithium aluminum hydride.

EXPERIMENTAL

2-Quinuclidine Carboxylic Dimethylamide

1.5 g of 2-quinuclidine carboxyl chloride was heated for 8 hours with 15 ml of thionyl chloride at 60-65°. The excess thionyl chloride was removed in vacuum, the remainder was removed by the two-fold addition of 20 ml of absolute benzene followed by its distillation. The 2-quinuclidine carboxyl chloride hydrochloride obtained was added gradually with cooling to 50 ml of 10% solution of dimethylamine in absolute ether. The reaction mixture was then shaken with 10 ml of a 50% solution of potassium carbonate, the ether solution was separated, dried with potassium carbonate, the solvent removed in vacuum, and the residue distilled at 0.34 mm. 0.8 g of a substance with a b.p. of 97-100° was obtained. The substance crystallized upon cooling in the form of white crystals with an m.p. of 48-50°. The yield was 57% of the theoretical. The substance was readily soluble in ether, chloroform, and alcohol, poorly in water.

4.089 mg substance: 9.901 mg CO_2; 3.586 mg H_2O. 6.790 mg substance: 7.42 ml 0.01 N H_2SO_4
Found %: C 66.08; H 9.81; N 15.30 $C_{10}H_{18}ON_2$. Calculated %: C 65.92; H 9.89; N 15.38.

2-Quinuclidine Carboxylic Diethylamide

The acid chloride obtained from 1.5 g of 2-quinuclidine carboxylic acid hydrochloride was treated in the manner reported above with a solution of 8.75 g of diethylamine in 15 ml of absolute benzene. 1.65 g of a substance with b.p. 100-102° at 0.35 mm was obtained. Yield, 75% of the theoretical amount. It was a colorless, oil-like liquid readily soluble in organic solvents and in water.

3.763 mg substance: 9.399 mg CO_2; 3.502 mg H_2O. 6.770 mg substance: 6.39 ml 0.01 N H_2SO_4.
5.666 mg substance: 5.32 ml 0.01 N H_2SO_4. Found %: C 68.16; H 10.41; N 13.21, 13.14.
$C_{12}H_{22}ON_2$. Calculated %: C 68.55; H 10.47; N 13.33.

[2-Carboxyquinuclidyl -(3)]-acetic Diamide

[2-Carboxyquinuclidyl -(3)]-acetyl dichloride hydrochloride, obtained from 3 g of the acid hydrochloride in the same manner as for 2-quinuclidine dicarboxylic acid hydrochloride, was suspended in 90 ml of absolute ether and the suspension saturated with ammonia. 40 ml of a 50% potassium carbonate solution was added to it, and it was well stirred. The precipitate, containing the diamide and a small amount of ammonium chloride, was filtered and air dried The residue was mixed with 50 ml of absolute alcohol, the alcoholic solution filtered from the insoluble ammonium chloride, decolorized with carbon, and evaporated to a volume of 15 ml. Upon cooling, 1.7 g of [2-carboxyquinuclidyl -(3)]-acetic diamide formed. M.p. 198-200°; yield, 66.8% of the theoretical. It was a white crystalline powder, readily soluble in water, soluble in alcohol upon heating, and insoluble in chloroform, acetone, ether, and benzene.

2.418 mg substance: 0.412 ml N_2 (22.5°, 747 mm). Found %: N 19.33. $C_{10}H_{17}O_2N_3$. Calculated %: N 19.9.

2-Carboxyquinuclidyl-(3)]-acetic Di-(dimethylamide)

[2-Carboxyquinuclidyl-(3)]-acetyl dichloride hydrochloride, obtained from 3 g of the acid hydrochloride, was treated with 45 ml of an 18% ether solution of dimethylamine. 2.56 g of a substance with b.p. 165-170° at 0.2 mm was obtained. Yield, 79.7% of the theoretical. The vacuum distilled product crystallized upon cooling; m.p. 117-118°. It was readily soluble in water, alcohol, chloroform, and acetone, difficultly in ether.

4.159 mg substance: 9.610 mg CO_2; 3.385 mg H_2O 5.436 mg substance: 6.23 ml 0.01 N H_2SO_4.
Found %: C 63.05; H 9.11; N 16.05. $C_{14}H_{25}O_2N_3$. Calculated %: C 62.92; H 9.36; N 15.72.

[2-Carboxyquinuclidyl-(3)]-Acetic Di-(diethylamide)

[2-Carboxyquinuclidyl-(3)]-acetyl dichloride hydrochloride, obtained from 3 g of the acid hydrochloride, was treated with a solution of 8.8 g of diethylamine in 20 ml of absolute benzene After the usual processing, 3.2 g of a substance with b.p. 163-165° at 0.4 mm was obtained. Yield, 82.2% of the theoretical. It was a viscous, yellow liquid which crystallized upon prolonged standing; m.p. 45°. The substance was readily soluble in water and in organic solvents.

4.448 mg substance; 10.921 mg CO_2; 4.069 mg H_2O. 3.265 mg substance: 3.10 ml 0.01 N H_2SO_4.
Found %: C 67.00; H 10.23; N 13.27. $C_{12}H_{22}O_2N_2$. Calculated %: C 66.87; H 10.41; N 13.00.

[2-Carboxyquinuclidyl-(3)]-acetic Dibenzylamide

[2-Carboxyquinuclidyl-(3)]-acetyl dichloride hydrochloride, obtained from 2 g of the acid hydrochloride, was added with stirring and cooling to a solution of 4.28 g of benzylamine in 40 ml of absolute ether. A voluminous precipitate, a mixture of [2-carboxyquinuclidyl-(3)]-acetic dibenzylamide and benzylamine hydrochloride formed. 40 ml of chloroform was added to the mixture to dissolve the dibenzylamide. Benzylamine hydrochloride was filtered and washed on the filter with another 40 ml of chloroform, the chloroform solution was evaporated in vacuum, and the dry residue was recrystallized from 10 ml of alcohol. 2.1 g of white crystals with m.p. 139-141° was obtained. Yield, 67.7% of the theoretical. The substance was readily soluble in chloroform, soluble in alcohol upon heating, poorly soluble in water, and insoluble in ether.

3.589 mg substance: 9.714 mg CO_2; 2.422 mg H_2O. 5.534 mg substance: 0.511 ml N_2 (22°, 729 mm).
Found %: C 73.86; H 7.55; N 10.24. $C_{24}H_{29}O_2N_3$. Calculated %: C 73.66; H 7.42; N 10.73.

2-Aminomethylquinuclidine

Because of the poor solubility of 2-quinuclidine carboxamide in ether [3], the reduction of the latter was conducted in a Tilepape extractor.

1.38 g of 2-quinuclidine carboxamide was placed in the cartridge. 85 ml of absolute ether and 0.85 g of lithium aluminum hydride were charged into the flask. The reaction mass was heated for 20 hours at a slow boil. At the end of the reaction, 1.34 ml of water was added with cooling to the flask. The precipitate of lithium and aluminum hydroxides which formed, was filtered, washed with chloroform, the precipitate transferred to a separatory funnel, 10 ml of a 50% solution of potassium carbonate was added, and it was extracted with chloroform. The chloroform extract was dried with potassium carbonate, the solvent was removed in vacuum, and the residue distilled at 83-85° at 5 mm. 0.5 g of a colorless oily substance was obtained which was readily soluble in organic solvents and in water. Yield, 40% of the theoretical.

4.990 mg substance: 6.95 ml 0.01 N H_2SO_4. Found %: N 19.49. $C_8H_{16}N_2$. Calculated %: N 20.20.

2-Aminomethylquinuclidine dihydrochloride was a white crystalline powder which was soluble in alcohol and water, and insoluble in ether, with m.p. 277-279° (from alcohol).

5.327 mg substance: 5.04 ml 0.01 N H_2SO_4. 6.060 mg substance: 8.281 mg AgCl. Found %: N 13.24; Cl 33.73. $C_8H_{18}N_2Cl_2$. Calculated %: N 13.14; Cl 33.33.

2-Dimethylaminomethylquinuclidine

A solution of 2 g of 2-quinuclidine carboxylic dimethylamide in 40 ml of absolute ether was gradually added with stirring to a solution of 1 g of lithium aluminum hydride in 40 ml of absolute ether. At the end of the addition, the reaction mixture was boiled for 20 hours, and then cooled, and 1.6 ml of water was added. The subsequent processing was the same as the above.

1.52 g of a substance with b.p. 89-90° at 7.5 mm was obtained. Yield, 82% of the theoretical. It was a colorless oil-like liquid readily soluble in organic solvents and in water.

2.940 mg substance: 3.43 ml 0.01 N H_2SO_4. 3.847 mg substance: 0.563 ml N_2 (25°, 737 mm).
Found %: N 16.30, 16.21. $C_{10}H_{20}N_2$. Calculated %: N 16.66.

2-Dimethylaminomethylquinuclidine dipicrate was a yellow crystalline substance with m.p. 211.5-213.5° (from alcohol).

4.561 mg substance: 7.129 mg CO_2; 1.743 mg H_2O. 4.268 mg substance: 6.651 mg CO_2; 1.703 mg H_2O.
2.190 mg substance: 2.78 ml 0.01 N H_2SO_4. Found %: C 42.65, 42.52; H 4.28, 4.46; N 17.77.
$C_{22}H_{26}O_4N_8$. Calculated %: C 42.17; H 4.15; N 17.89.

2-Diethylaminomethylquinuclidine

3.22 g of 2-quinuclidine carboxylic diethylamide was reduced with 1 g of lithium aluminum hydride in 40 ml of ether. 2.44 g of a substance with b.p. 131-132° was obtained. Yield 81% of the theoretical. It was a syrupy colorless liquid soluble in organic solvents and in water.

3.539 mg substance: 0.443 ml N_2 (22°, 760 mm). Found %: N 13.68. $C_{12}H_{24}N_2$. Calculated %: N 13.77.

2-Diethylaminomethylquinuclidine dipicrate was a yellow crystalline substance with m.p. 196-198° (from 50% alcohol).

4.19 mg substance: 7.128 mg CO_2; 1.759 mg H_2O. 4.240 mg substance: 6.842 mg CO_2; 1.771 mg H_2O.
4.168 mg substance: 5.17 ml 0.01 N H_2SO_4. Found %: C 44.02, 44.04; H 4.45, 4.68; N 17.36.
$C_{24}H_{30}O_{14}N_8$. Calculated %: C 44.03; H 4.58; N 17.12.

2-Dimethylaminomethyl-3-(β-dimethylaminoethyl)-quinuclidine

2.4 g of [2-carboxyquinuclidyl-(3)]acetic di-(dimethylamide) was reduced with 1.5 g of lithium aluminum hydride in a mixture of 30 ml of ether and 30 ml of benzene. 1.64 g of a substance with b.p. 98° at 0.3 mm was obtained. Yield, 76.3% of the theoretical. It was a colorless, mobile liquid, readily soluble in water and organic solvents.

2.965 mg substance: 0.470 ml N_2 (23.5°, 724 mm). Found %: N 17.39. $C_{14}H_{29}N_3$. Calculated %: N 17.57.

2-Dimethylaminomethyl-3-(β-dimethylaminoethyl)-quinuclidine tripicrate was a yellow crystalline substance with m.p. 196-197° (from acetone).

3.120 mg substance: 4.720 mg CO_2; 1.134 mg H_2O 3.027 mg substance: 3.95 ml 0.01 N H_2SO_4.
Found %: C 41.55; H 4.06; N 18.27. $C_{32}H_{38}O_{21}N_{12}$. Calculated %: C 41.47; H 4.10; N 18.12.

2-Diethylaminomethyl-3-(β-diethylaminoethyl)-quinuclidine

1.3 g of [2-carboxyquinuclidyl-(3)]acetic di-(diethylamide) was reduced in 30 ml of dry ether. 0.95 g of a substance with b.p. 125-127° at 0.26 mm was obtained. Yield, 80.7% of the theoretical. It was a colorless, lively liquid readily soluble in water and in organic solvents.

4.035 mg substance: 10.867 mg CO_2; 4.625 mg H_2O. 4.300 mg substance: 11.538 mg CO_2; 4.809 mg H_2O.
2.632 mg substance: 0.343 ml N_2 (20°, 726 mm). 2.713 mg substance: 0.348 ml N_2 (23°, 728 mm).
Found %: C 73.49, 73.23; H 12.82, 12.51; N 14.50, 14.17. $C_{18}H_{37}N_3$. Calculated %: C 73.22; H 12.54; N 14.24.

2-Benzylaminomethyl-3-(β-benzylaminoethyl)-quinuclidine

1.16 g of a substance with b p. 230-232° at 0.3 mm was obtained by the reduction of 1.72 g of [2-carboxyquinuclidyl-(3)]-acetic dibenzylamide by the action of 0.8 g of lithium aluminum hydride in 100 ml of absolute benzene. Yield, 72 % of the theoretical. It was a viscous, yellow liquid, readily soluble in water and organic solvents.

4.482 mg substance: 12.869 mg CO_2; 3.605 mg H_2O. 5.407 mg substance: 15.596 mg CO_2; 4.260 mg H_2O. Found %: C 78.35, 78.71; H 9.00, 8.82. $C_{24}H_{33}N_3$. Calculated %: C 78.74; H 9.1.

SUMMARY

A series of substituted 2-aminomethylquinuclidines and 2-aminomethyl-3-(β-aminoethyl)-quinuclidines was synthesized.

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INVESTIGATION OF COMPOUNDS CONTAINING A THREE-MEMBERED OXIDE RING

VI. REACTION OF ETHYL β-METHYL-β-ETHYLGLYCIDATE WITH ANILINE

V. F. Martynov and Ya. A. Kastron

The results of the reaction between ethyl β,β-dimethylglycidate and aniline and its homologs were reported in the previous communications. It was shown that in all cases the oxide ring of the above glycidic acids was opened from the side of the β-carbon atom, and a β-arylamino substituted α-hydroxyisovaleric acid is formed.

The present study is an extension of the above investigation. The reaction between the ethyl glycidate and the aniline was effected, as in the previous cases, by heating a mixture of the two at 170-180°, in a sealed tube.

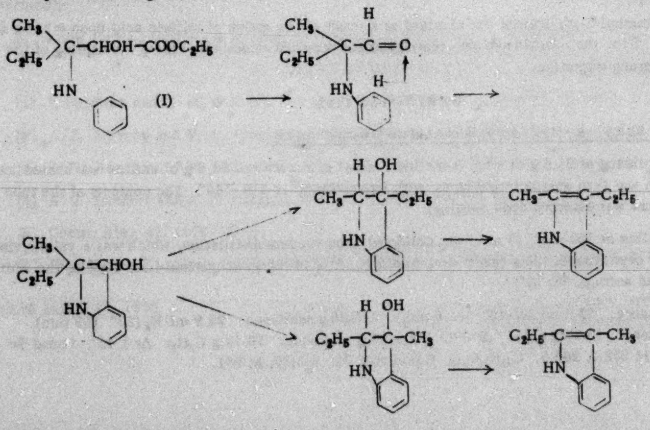
The investigation showed that the oxide of β-methyl-β-ethylglycidic acid was considerably more stable than that of β,β-dimethylglycidic acid; the addition of aniline proceeded with considerably more difficulty in the first case than in the second.

The heating of ethyl β-methyl-β-ethylglycidate with aniline for 6 hours at the above temperature led to only a 20% yield of the addition product, while under analogous conditions, ethyl dimethylglycidate formed an addition product with a 60% yield with aniline.

In order to attain a satisfactory yield of the reaction product, it was found necessary to increase the heating time of the reaction mixture sharply. Thus, a 50% yield could only be obtained by a 50-hour heating. Such a sharp difference in the reactivity of the above glycidic acids is explained, possibly, by the increased steric hindrance upon changing the methyl group to an ethyl group on the β-carbon atom.

The product of the addition of aniline to ethyl β-methyl-β-ethyl-glycidate was a crystalline compound to which, on the basis of the previously conducted investigations, the formula of ethyl α-hydroxy-β-aninilinoisocaproate (I) could be assigned with a great degree of certainty.

For a conclusive proof of the certainty of this formula, the compound obtained was heated with strong sulfuric acid. An intense evolution of carbon monoxide occurred at 110-115° which, as is known, is a property of α-hydroxy acids. The second fragment of the molecule, under such a decomposition, must have been the corresponding amino aldehyde which could not have remained unchanged under the conditions of the given reaction, and which must have been, judging from previous studies, converted into methylethylindole. However, the formation of two isomeric methylethylindoles should have been expected upon the closing of the indole ring in this case. The isomerism can be illustrated by the following scheme:



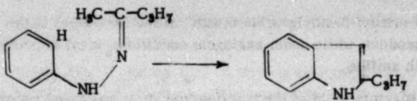
As is apparent from the given scheme, 2-methyl-3-ethylindole, 3-methyl-2-ethylindole, or a mixture of the two isomers could have been obtained as a result of the above transformations. Both isomeric indoles are known from the literature. 3-Methyl-2-ethylindole is a solid with a melting point, according to one literature reference, of 66° [1], and 59°, according to another [2]. 2-Methyl-3-ethylindole, according to one reference, is a liquid with b.p. 291-293° (750 mm) [3, 4], and a crystalline compound with m.p. 44-45°, according to another [5].

A crystalline compound with a strong fecal odor and m.p. of 44.5-45° was obtained. All analyses upheld the formula of methylethylindole for it.

Therefore, this investigation showed, without any doubt, that the opening of the oxide ring by the action of aniline occurs from the side of the β-carbon atom for ethyl-β-methyl-β-ethylglycidate. The addition product must be assigned the structure ethyl α-hydroxy-β-anilino-isocaproate

In addition it was necessary to prove the structure of the methylethylindole obtained. This problem was complicated by the fact that, as was shown above, there was disagreement on the physical constants of 2-methyl-3-ethylindole, and therefore, there was no rigidly established standard for comparison.

Such a disagreement in the physical properties of 2-methyl-3-ethylindole can be explained by the method of its preparation. All of the authors started with Fischer's method, i.e., the decomposition of the methylpropyl ketone phenylhydrazone, whereby they believed that the reaction proceeds only in one direction, the formation of 2-methyl-3-ethylindole, and completely neglected the second possibility of the formation of 2-propylindole.



even though the reaction undoubtedly occurred.

It is not surprising, therefore, that 2-methyl-3-ethylindole was characterized until recently as a liquid. The small impurity of propylindole sharply lowered the melting point. Only in 1947 was a pure preparation of crystalline structure obtained [5].

In order to prove the structure of the methylethylindole obtained, both of the possible isomers were synthesized; 2-methyl-3-ethyl indole, synthesized by Fischer's method, was a liquid. The mixed melting point of the compound obtained with the crystalline isomer of 3-methyl-2-ethylindole gave a strong depression. This served as an indirect proof that the isomeric 2-methyl-3-ethylindole was obtained.

For final proof, picrates of both isomeric indoles were obtained, and a mixed melting point of the two was initially taken; a large depression occurred. Then mixed melting points of the picrate of the methylethylindole obtained with those of the two isomeric forms of methylethylindole were taken. A depression was absent only upon melting with 2-methyl-3-ethylindole picrate.

Therefore, 2-methyl-3-ethylindole was obtained as a result of the action of sulfuric acid upon ethyl-α-hydroxy-β-anilinoisocaproate. Thus, the retropinacoline rearrangement occurred selectively during the closing of the indole ring, with the ethyl group migrating.

EXPERIMENTAL

Preparation of Ethyl-α-Hydroxy-β-anilinoisocaproate

A mixture consisting of 31.6 g of ethyl β-methyl-β-ethyl glycidate and 55.8 g of aniline was sealed into a glass ampoule, which was then heated for 40 hours (with interruptions) at 170-180°. The contents of the tube turned red, and some pressure was detected upon opening.

A fraction boiling at 150-154° (3 mm) was collected upon vacuum distillation, which was a yellow, viscous liquid which rapidly crystallized. 25 g (50%) was obtained. After 4 recrystallizations from ligroin, the white crystalline compound had an m.p. 59-60°.

0.4686 g substance: 22.6 ml N_2 (19°, 761.5 mm). 0.4435 g substance: 22.9 ml N_2 (20°, 759 mm). 0.1500 g substance; 15.26 g C_6H_6 Δt 0.20°. 0.9454 g substance: 13.70 g C_6H_6: Δt 1.42°. Found %: N 5.18, 5.30; M 252.1, 248.8. $C_{14}H_{21}O_3N$. Calculated %: N 5.57, M 251.

For the determination of carbon monoxide during the decomposition of ethyl α-hydroxy-β-anilinoisocaproate by the action of concentrated sulfuric acid, an apparatus and procedure was used which was applied for the analysis of tertiary and secondary fatty acids [6].

The heating with sulfuric acid was conducted at 110-115°, i.e., at that temperature at which the decomposition of the secondary, indole, component of the reaction did not occur.

0.3890 g substance: 34.5 ml CO (17°, 756.5 mm). 0.4156 g substance: 38.3 ml CO (17°, 756.5 mm).
Found %: CO 11.09, 11.50. $C_{14}H_{21}O_3N$. Calculated %: CO 11.15.

Transformation of Ethyl α-Hydroxy-β-anilinoisocaproate into 2-Methyl-3-ethylindole

15 g of ethyl α-hydroxy-β-anilinoisocaproate was added to 50 ml of concentrated sulfuric acid; a complete solution occurred with shaking and slight heating. At 95° (thermometer within the mixture), the formation of gas bubbles started to occur (carbon monoxide). At 110-115° there was an intense evolution of carbon monoxide. After the end of the evolution of the gas, the red colored liquid was poured into water with ice, and the acid neutralized with alkali. The substance which formed as an emulsion was extracted with ether. After the usual operations and the removal of the ether, 4.5 ml of a red brown liquid was obtained The substance distilled in vacuum at 117.5-118° (2 mm), and was a light yellow liquid of average viscosity which rapidly crystallized. 4 g, which was 42%, was obtained. The yield of the product should have been higher since no tarring had occurred, but 2-methyl-3-ethylindole possesses a noticeable solubility, which was mentioned by other authors [3], because of which, evidently, some decrease of the yield occurred. After recrystallization from petroleum ether, the m.p. was 44-44.5°.

Found %: N 9.0; OH 10.9; M 157.7. $C_{11}H_{13}N$. Calculated %: N 8.8; OH 10.7; M 159.

The picrate (wine-red thin needles) melted at 150-151° after recrystallization from aqueous alcohol. Literature data: 152-153° [3], 148-149° [5]. A mixed melting point determination with 2-methyl-3-ethylindole which was obtained and authentically synthesized 3-methyl-2-ethylindole gave a m.p. of 26-28° which was a depression of 17° from the lower melting point.

A mixed melting point determination of 2-methyl-3-ethylindole picrate and 3-methyl-2-ethylindole picrate gave a m.p. 128-130°; depression, ≈20°. A mixed, melting point determination of 2-methyl-3-ethylindole picrate obtained and that of 3-methyl-2-ethylindole synthesized authentically, gave a m.p. of 131-132°; depression, ≈20°. No depression was found in a mixed melting point determination of 2-methyl-3-ethylindole picrate obtained and authentically synthesized 2-methyl-3-ethylindole picrate (m.p. 150°).

SUMMARY

1. The reaction between ethyl β-methyl β-ethylglycidate with aniline was studied. It was shown that the opening of the epoxy ring of the above glycidic acid occurs at the side of the β-carbon atom under the action of aniline. Ethyl α-hydroxy-β-anilinoisocaproate, unreported hitherto in the literature, was obtained.

2. The ease of selective retropinacolin rearrangement was studied on the example of the preparation of 2-methyl-3-ethylindole

3. A new method for the preparation of 2-methyl-3-ethylindole was developed.

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The A. A. Zhdanov Leningrad State University,
Awarded the Order of Lenin.

SYNTHETIC INVESTIGATIONS OF INDOLE DERIVATIVES

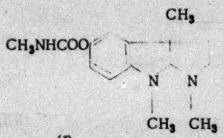
I. SYNTHESIS OF 1-METHYL-5-HYDROXYINDOLINE AND 1,3-DIMETHYL-5-HYDROXYINDOLINE (DIHYDROPHYSOSTIGMOL) URETHANES

M. N. Kolosov and N. A. Preobrazhensky

The heterocyclic indole (2,3-benzopyrrole) system is of considerable interest as a structural basis of a large number of natural and synthetic substances having important scientific and practical value. The number of indole derivatives also includes such important therapeutic alkaloids as eserine (physostigmine), strychnine, yohimbine, cinchonamine, ergotoxin, ergotamine, and others, growth factors such as indolylacetic acid, as well as natural and synthetic dyes such as indigo.

This paper is the first communication of a series on investigations of natural indole compounds and their synthetic analogs.

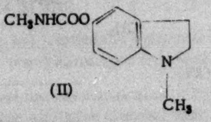
The alkaloid eserine (physostigmine), the active principle in the fruit of the tropical plant Physostigma venenosum (the so-called calabar bean) is the strongest parasympathomimetic substance which blocks chioline esterase. Because of its exceptionally strong physiological activity, eserine has a wide application in medicine and veterinary medicine, as well as in biological investigations. It is used mainly as an agent for the lowering of intraocular pressure and as a miotic agent antagonistic to atropine and curarine. The effect of eserine and its analogs (for example proeserine) on the cholinesterase system has found great application recently, especially in the therapy of diseases due to the disruption of the peripheral, as well as the central, nervous system. However, eserine possesses certain drawbacks as a therapeutic agent: it is unstable in aqueous solutions, the organism acquires a rapid tolerance to the preparation which makes an increase of the amount of the substance used necessary. In doses greater than the therapeutic, eserine is very toxic, its largest single dose being only 0.001 g, and the lethal, 0.003 g.



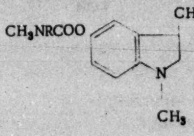
(I)

Because of the valuable physiological action of the alkaloid eserine (physostigmine) (I), it is of undoubted interest to prepare simpler substances containing the elements of its structure, as well as to determine the value of the separate elements of this structure in the above substances for the presence of physiological action. The main interest lies in a search for those analogs of eserine which would lack the above drawbacks. After a definite relation between the physiological activity of eserine and the presence of the methylurethane (methylcarbamyl) group in its structure had been established [1], the main direction in the search for synthetic substitutes for eserine was the preparation of various methylurethanes of aromatic aminophenols, and at the present time, the corresponding pyridine derivatives.* However, there have been no modifications effected up to now in the structure of eserine itself, and especially in its heterocyclic part, in order to improve the therapeutic properties of this substance.

The synthesis of the simplest indole analog of the alkaloid eserine, 1-methyl-5-hydroxyindoline methylurethane (II), as well as 1,3-dimethyl-5-hydroxyindoline (dihydrophysostigmol) mono and dimethylurethanes (III) and (IV) is reported in the present communication. In contrast to eserine, these substances do not contain a second pyrrolidine ring in their structures.



(II)



(III) R = H;
(IV) R = CH_3.

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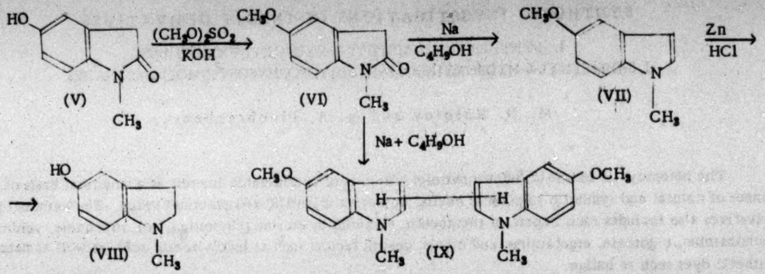
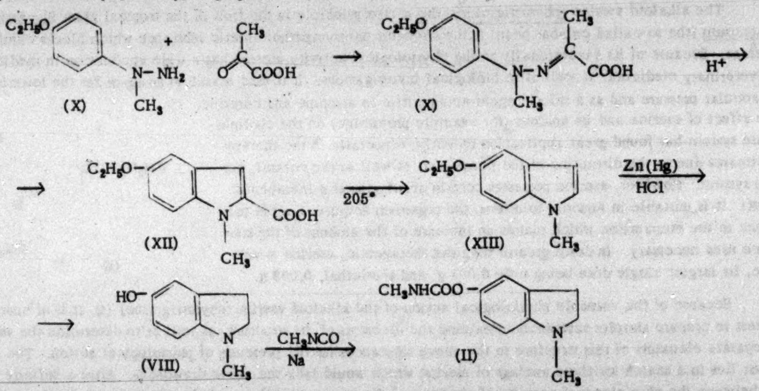
* See monograph [2], as well as a more recent paper [3].

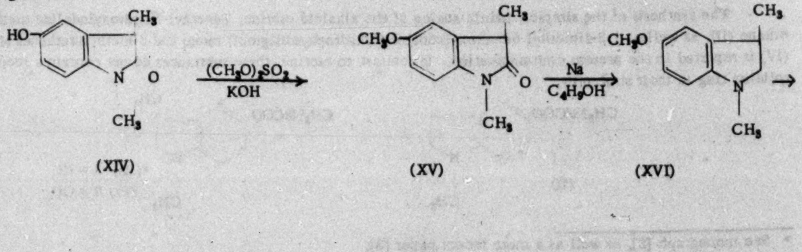
During an attempt to prepare the necessary 1-methyl-5-hydroxyindoline (VIII) from 1-methyl-5-hydroxyindoline-2-one (V), reported in the literature [4], according to the scheme shown below, it was found that the reduction of the hydroxyindole (VI) with sodium in butanol led to the condensation of 2 molecules, because of which the diindolyl derivative (IX) was obtained instead of the expected 1-methyl-5-methoxyindole (VII):

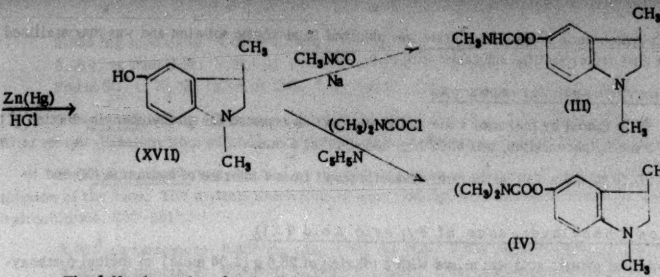


For this reason, a different route was used for the synthesis of 1-methyl-5-hydroxyindoline urethane (II) starting from N-methyl-p-ethoxyphenylhydrazine (X):



The first scheme proved quite satisfactory for the preparation of 1,3-dimethyl-5-hydroxyindoline (dihydrophysostigmol) since 1,3-dimethyl-5-methoxyindoline-2-one (XV) gave physostigmol methyl ether (XVI) in good yield upon treatment with sodium and butyl alcohol. Therefore, the successful synthesis of the mono- and dimethylurethanes of 1,3-dimethyl-5-hydroxyindoline (dihydrophysostigmol) (III and IV) can be expressed by the following scheme:





The following values for the threshhold concentrations of substances were obtained by a study of the miotic action upon rabbits of the analogs of serine reported in the present communication*: hydrochloride (II) – 1:2000, methiodide (II) – 1:1000, hydrochloride (III) – 1:100,000, methiodide (III) – less than 1:1000, hydrochloride (IV) – less than 1:1000, and methiodide (IV) – less than 1:1000.

EXPERIMENTAL

1. 1-Methyl-5-methoxyindoline-2-one (VI).

9.4 g (1.00 mole) of technical 1-methyl-5-hydroxyindoline-2-one [4] was dissolved in 80 ml of a 5% solution of potassium hydroxide, filtered from tars, and 7.5 g (1.03 moles) of dimethyl sulfate added with stirring. The mixture was heated on the water bath for 1 hour, keeping an alkaline reaction by further addition of 5% potassium hydroxide solution. The dense oil which separated upon cooling, was extracted with chloroform, the extracts dried with sodium sulfate, and the solvent removed. The residue was distilled and 6.4 g (62.7%) of 1-methyl-5-methoxyindoline-2-one with b.p. 132-136° at 1 mm was obtained. It melted at 96-97° [5] after recrystallization from an ether methanol mixture.

2.990 mg substance: 7.430 mg CO_2; 1.630 mg H_2O. 3.015 mg substance: 7.490 mg CO_2; 1.575 mg H_2O.
2.565 mg substance: 0.181 ml N_2 (24°, 731 mm). 3.520 mg substance: 0.245 ml N_2 (25°, 745 mm).
Found %: C 67.76, 67.70; H 6.10, 6.20; N 7.78, 7.81. $C_{10}H_{11}O_2N$. Calculated %: C 67.76; H 6.26; N 7.91.

2. Reduction of 1-Methyl-5-methoxyindoline-2-one

17 g (20.5 g atoms) of sodium was added to a boiling solution of 6.4 g (1.00 mole) of 1-methyl-5-methoxyindoline-2-one in 200 ml of butyl alcohol. The reaction mass was heated to reflux until the start of precipitation of sodium butylate, then 50 ml of butanol was added, and the heating was continued until complete solution of the sodium. Upon cooling, the solution was wahed several times with ice water, and the alcohol removed in vacuum. The residue was shaken with 30 ml of water and 20 ml of ether, the crystals which separated (A), were filtered; they weighed 14 g (24.2%) The ether solution was washed with water, dried with sodium sulfate, the ether removed, and residue distilled in vacuum. The fraction 130-160° at 2 mm obtained crystallized After recrystallization from an ether-methanol mixture, 2.0 g (31.3%) of a substance with m.p 96-97° was obtained, which did not give depression in a mixed melting point determination with the starting 1-methyl-5-methoxyindoline-2-one.

Substance A was a white crystalline material with an m.p. of 136-136.5° after two recrystallizations from alcohol using carbon.

3.035 mg substance: 8.365 mg CO_2; 1.670 mg H_2O. 3.000 mg substance: 8.250 mg CO_2; 1.665 mg H_2O
3.195 mg substance: 0.250 ml N_2 (24°, 746 mm). 3.295 mg substance: 0.250 ml N_2 (24°, 753 mm).
5.375 mg substance; 63.0 mg camphor: Δt 11.13°, 4.035 mg substance; 36.9 mg camphor: Δt 14.13°.
Found %: C 75.16, 74.90; H 6.16, 6.21; N 8.83, 8.64; M 307, 310. $C_{10}H_{20}O_2N_2$. Calculated %: C 74.96; H 6.30; N 8.74; M 320.

The substance was insoluble in water and in aqueous alkali solutions; it dissolved in cold concentrated hydrochloric acid but precipitated upon the addition of water. The compound gave a wine-red color with a pine splinter moistened with hydrochloric acid. The picrate was obtained in alcoholic solution and was recrystallized from alcohol. It was a dark red crystalline substance with m.p. 109°.

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* The investigation of the physiological activity of the substances synthesized in the present study was conducted in the S. Ordzhonikidze All-Union Chemico-Pharmaceutical Scientific Research Institute by the students of co-worker I. M. Sharapov under the direction of Prof. M. D. Mashkovsky to whom the authors wish to express their sincerest appreciation.

3. Methyl-p-ethoxyphenylhydrazine (X)

This substance was prepared by means of a method similar to that reported for methylphenylhydrazine [6]. The yield, based upon N-methylphenetidine, was 55%, b.p. 137-140° at 6 mm.

Literature data (7) (b.p. about 140° at 12 mm) evidently result from a mixture of hydrazine (X) and N-methylphenetidine.

4. Methyl-p-ethoxyphenylhydrazone of Pyruvic Acid (XI)

17.0 g (1.25 moles) of pyruvic acid was mixed with a solution of 25.6 g (1.00 mole) of methyl-p-ethoxyphenylhydrazine in 75 ml of 50% acetic acid. After standing for 2 hours at room temperature, the reaction mixture was cooled and the crystals which separated were filtered and washed with cold 50% acetic acid and water. After drying in vacuum, 32.8 g (90.3%) of pyruvic acid methyl-p-ethoxyphenylhydrazone with m.p. 68-70° was obtained. The substance melted at 70.5-71.0° after recrystallization from aqueous methyl alcohol, and was a yellowish crystalline substance, very readily soluble in the usual organic solvents.

2.935 mg substance: 6.580 mg CO$_2$; 1.760 mg H$_2$O. 3.020 mg substance: 6.740 mg CO$_2$; 1.800 mg H$_2$O. 2.710 mg substance: 0.294 ml N$_2$ (25°, 724 mm). 2.825 mg substance: 0.315 ml N$_2$ (25°, 720 mm). Found %: C 61.14, 60.86; H 6.71, 6.67; N 11.82, 12.10. C$_{12}$H$_{16}$O$_3$N$_2$. Calculated %: C 60.98; H 6.83; N 11.86.

5. 1-Methyl-2-carboxy-5-ethoxyindole (XII)

A solution of 32.8 g of pyruvic acid methyl-p-ethoxyphenylhydrazone in 165 ml of glacial acetic acid was heated for 5 minutes at 60-65°, and then 165 ml of water was added, and the reaction mass was heated for 15 minutes more at 60°. The precipitate which formed upon cooling was filtered, the filtrate was diluted with a large amount of water and heated to boiling. The crystals which separated upon cooling were filtered, combined with those previously obtained, and dried in vacuum over potassium hydroxide. 12.6 g (41.4%) of 1-methyl-2-carboxy-5-ethoxyindole with m.p. 185-187° (with decomposition) was obtained. After several recrystallizations from alcohol with carbon, the substance was obtained in the form of colorless needles with m.p. 188° (with decomposition).

3.100 mg substance: 7.460 mg CO$_2$; 1.735 mg H$_2$O. 3.010 mg substance: 7.225 mg CO$_2$; 1.650 mg H$_2$O 5.445 mg substance: 0.314 ml N$_2$ (22°, 740 mm). 5.485 mg substance: 0.324 ml N$_2$ (22°, 740 mm). Found %: C 65.63, 65.46; H 6.26, 6.13; N 6.50, 6.66. C$_{12}$H$_{13}$O$_3$N. Calculated %: C 65.72; H 5.98; N 6.39.

6. 1-Methyl-5-ethoxyindole (XIII).

12.6 g of technical 1-methyl-2-carboxy-5-ethoxyindole was heated to 205-210° on a metal bath until the evolution of carbon dioxide stopped (about 40 minutes), and the 1-methyl-5-ethoxyindole formed vacuum distilled; the distillate crystallized rapidly. 8.7 g of a colorless substance with b.p. 145-148° at 7 mm and m.p. 82-85° was obtained. Yield, 86.5% After recrystallization from ether, crystals, with m.p. 85-86° [8] were obtained.

3.050 mg substance: 8.450 mg CO$_2$; 1.990 mg H$_2$O. 3.015 mg substance: 8.370 mg CO$_2$; 2.010 mg H$_2$O. 3.975 mg substance: 0.294 ml N$_2$ (25°, 730 mm). 3.470 mg substance: 0.254 ml N$_2$ (25°, 730 mm). Found %: C 75.55, 75.70; H 7.30, 7.46; N 8.13, 8.05. C$_{11}$H$_{13}$ON. Calculated %: C 75.38; H 7.48; N 8.00.

The picrate crystallized from alcohol in the form of dark red scales with m.p. 96.0-96.5°.

7. 1-Methyl-5-hydroxyindoline (VIII)

8.7 g of 1-methyl-5-ethoxyindole was added to 90 g of finely granulated amalgamated zinc in 200 ml of concentrated hydrochloric acid. The reaction mass was refluxed for 9 hours while a stream of hydrogen chloride was passed in, and then for 2 hours more. Upon cooling, the light yellow solution was decanted from the residue, and neutralized with solid sodium bicarbonate. The free base was extracted with ether, the extracts evaporated to approximately 100 ml, washed with water, and dried with sodium sulfate The residue after the removal of the ether. was distilled, and 2.89 g (39.0%) of colorless, 1-methyl-5-hydroxyindoline with b.p. 120-122 at 1 mm and m.p. 79-81° was obtained. After recrystallization from ether, the substance was a white powder with m.p. 83-84°; a mixture with 1-methyl-5-ethoxyindole melted at 63-65°.

3.035 mg substance: 8.050 mg CO_2; 2.020 mg H_2O. 3.000 mg substance: 7.980 mg CO_2; 1.990 mg H_2O. 3.660 mg substance: 0.324 ml N_2 (24°, 730 mm). 2.320 mg substance: 0.201 ml N_2 (24°, 730 mm). Found %: C 72.33, 72.53; H 7.45, 7.42; N 9.77, 9.56. $C_9H_{11}ON$. Calculated %: C 72.43; H 7.44; N 9.39.

The picrate was obtained upon mixing hot concentrated solutions of the base and picric acid in alcohol. After recrystallization from ethanol, bright yellow crystals with m.p. 154-155° (with decomposition) were obtained.

The hydrochloride was obtained by the addition of an alcoholic hydrogen chloride solution to a hot alcoholic solution of the base. The crystals which formed upon cooling, were recrystallized from absolute alcohol; m.p. of the hydrochloride, 200-201°.

3.085 mg substance: 6.620 mg CO_2; 1.755 mg H_2O. 3.010 mg substance: 6.450 mg CO_2; 1.725 mg H_2O. 3.750 mg substance: 0.260 ml N_2 (25°, 731 mm). 3.920 mg substance: 0.274 ml N_2 (25°, 731 mm). Found %: C 58.51, 58.43; H 6.36, 6.41; N 7.64, 7.70. $C_9H_{12}ONCl$. Calculated %: C 58.23; H 6.52; N 7.54.

8. 1-Methyl-5-hydroxyindoline Methylurethane (II)

1 mg of sodium was added to a solution of 2.89 g (1.00 mole) of 1-methyl-5-hydroxyindoline in 20 ml of absolute benzene, and when the evolution of hydrogen had stopped, a solution of 2.8 g (2.53 moles) of methyl isocyanate (b.p. 39-41°) [11] in 6 ml of absolute benzene was added. The mixture was left to stand for three days in a tightly stoppered bottle at room temperature, filtered from a small amount of a residue, and evaporated in vacuum. After recrystallization of the residue from ether, 3.34 g (83.6%) of colorless 1-methyl-5-hydroxyindoline methylurethane with m.p. 95.5-96.5° was obtained; a mixture with 1-methyl-5-hydroxyindoline melted at 53-57°.

3.135 mg substance: 7.390 mg CO_2; 1.910 mg H_2O. 3.010 mg substance: 7.090 mg CO_2; 1.850 mg H_2O. 2.695 mg substance: 0.324 ml N_2 (25°, 745 mm). 2.320 mg substance: 0.274 ml N_2 (23°, 748 mm). Found %: C 64.28, 64.24; H 6.82, 6.88; N 13.50, 13.40. $C_{11}H_{14}O_2N_2$ Calculated %: C 64.04; H 6.86; N 13.58.

The picrate melted at 138-139° after recrystallization from alcohol.

The hydrochloride was obtained from an ethereal solution of the base and an alcohol solution of hydrogen chloride. After recrystallization from butyl alcohol, a white powder with m.p. 152-153° was obtained.

3.025 mg substance: 6.055 mg CO_2; 1.625 mg H_2O. 2.995 mg substance: 5.955 mg CO_2; 1.615 mg H_2O. 1.910 mg substance: 0.196 ml N_2 (24°, 746 mm). 2.285 mg substance: 0.235 ml N_2 (24°, 746 mm). Found %: C 54.58, 54.22; H 6.01, 6.03; N 11.58, 11.61. $C_{11}H_{15}O_2N_2Cl$. Calculated %: C 54.41; H 6.23; N 11.54.

The methiodide was obtained in ethereal solution and recrystallized from absolute butanol; colorless crystals with m.p. 205-206° were obtained.

9. 1,3-Dimethyl-5-methoxyindoline-2-one (XV).

It was obtained from technical 1,3-dimethyl-5-hydroxyindole [9] with a yield of 65% by means of a method analogous to that reported above for the synthesis of 1-methyl-5-methoxyindoline-2-one (VI). After recrystallization from ether, it had a m.p. of 86° and a b.p. of 180-182° at 15 mm.

2.985 mg substance: 7.585 mg CO_2; 1.845 mg H_2O 3.650 mg substance: 0.245 ml N_2 (20°, 744 mm). Found %: C 69.29; H 6.91; N 7.65. $C_{11}H_{13}O_2N$. Calculated %: C 69.08; H 6.85; N 7.33

10. 1,3-Dimethyl-5-methoxyindole (XVI) (Physostigmol Methyl Ether)

15 g (1 mole) of 1,3-dimethyl-5-methoxyindoline-2-one was reduced with 50 g (27.6 g atoms) of sodium in 500 ml of absolute butyl alcohol in the same manner as reported for 1-methyl-5-methoxyindoline-2-one. The residue, after the removal of the alcohol, was dissolved in 50 ml of chloroform, the solution washed with water, the solvent removed, and the residue distilled. 10.9 g of a substance with b.p. 159-162° at 14 mm was obtained Yield, 9.3%. After recrystallization from ether, the m.p. was 60-61° [10].

The picrate was prepared in alcoholic solution and recrystallized from alcohol. It was a dark red crystalline substance with m.p. 116-117°.

11. 1,3-Dimethyl-5-hydroxyindoline (XVII) (Dihydrophysostigmol)

10.9 g of physostigmol methyl ether, 100 g of amalgamated zinc, and 250 ml of concentrated hydrochloric acid were heated under the conditions reported for the preparation of 1-methyl-5-hydroxyindoline. The residue after evaporation of the ether extract crystallized. It was washed from an oil-like impurity with cold chloroform, and 5.18 g (51.0%) of colorless dihydrophysostigmol with m.p. 92-94° was obtained After recrystallization from ether, it had an m.p. 99°.

3.015 mg substance: 8.100 mg CO_2; 2.180 mg H_2O. 4.130 mg substance: 0.324 ml N_2 (21°, 735 mm). Found %: C 73.26; H 8.09; N 8.80. $C_{10}H_{13}ON$. Calculated %: C 73.62; H 8.04; N 8.59.

The picrate was obtained in the usual manner and recrystallized from alcohol; it had a m.p. of 165-166°.

The hydrochloride was prepared in ether solution. It crystallized from ethanol in the form of colorless crystals with a m.p. of 169-170°.

2.915 mg substance: 6.455 mg CO_2; 1.870 mg H_2O. 3.160 mg substance: 7.020 mg CO_2; 2.050 mg H_2O 4.885 mg substance: 0.324 ml N_2 (21°, 724 mm). 4.090 mg substance: 0.264 ml N_2 (25°, 728 mm). Found %: C 60.39, 60.58; H 7.18, 7.26; N 7.33, 7.08. $C_{10}H_{14}ONCl$. Calculated %: C 60.32; H 7.08; N 7.03.

12. 1,3-Dimethyl-5-hydroxyindoline Methylurethane (III) (Dihydrophysostigmol Methylurethane).

1 mg of sodium was added to a solution of 2.0 g (1.00 mole) dihydrophysostigmol in 20 ml of absolute benzene, and after the evolution of hydrogen stopped, 1.7 g (2.43 moles) of methyl isocyanate [11] in 10 ml of benzene. After standing for 24 hours at room temperature, the solution was filtered and evaporated in vacuum. The residue crystallized slowly. After recrystallization from 60% alcohol, 2.26 g (83.7%) of colorless, dihydrophysostigmol methylurethane with m.p. 75-76° was obtained A mixture with dihydrophysostigmol melted at 48-52°.

2.970 mg substance: 7.130 mg CO_2; 1.910 mg H_2O. 3.040 mg substance: 0.358 ml N_2 (25°, 734 mm). Found %: C 65.46; H 7.20; N 13.04. $C_{12}H_{16}O_2N_2$. Calculated %: C 65.45; H 7.33; N 12.73.

The picrate was obtained in alcoholic solution and recrystallized from 80% alcohol. It had a m.p. of 127°; a mixture with picric acid melted at 92-94°.

The methiodide was obtained from a methanolic solution with excess of methyl iodide. After recrystallization from alcohol colorless crystals with m.p. 178.0-178.5° (with decomposition) were obtained.

The hydrochloride was obtained from an ethereal solution of the base and an alcoholic hydrogen chloride solution; it crystallized from alcohol in the form of colorless prisms with m.p. 168-168.5° (with decomposition).

2.955 mg substance: 6.090 mg CO_2; 1.700 mg H_2O. 3.650 mg substance: 0.362 ml N_2 (22°, 724 mm). Found %: C 55.86; H 6.44; N 10.93. $C_{12}H_{17}O_2N_2Cl$. Calculated %: C 56.12; H 6.68; N 10.91.

13. 1,3-Dimethyl-5-hydroxyindoline Dimethylurethane (IV) (Dihydrophysostigmol Dimethylurethane) ,

2.0 g (1.00 mole) dihydrophysostigmol, 4.0 g (3.03 moles) of dimethylcarbamyl chloride (b.p. 165.5-166.5°), and 10 ml of dry pyridine was heated for 3 hours on a metal bath at 140-145°. Upon cooling the reaction mass was evaporated in vacuum, 10 ml of water was added, and again evaporated. This operation was repeated 3-4 times more, and then 40 ml of ether and 20 ml of a 10% potassium hydroxide solution were added. The ether solution was washed with water, dried, and the ether removed. 1.5 ml of 20% hydrochloric acid was added and the mixture left in vacuum over potassium hydroxide until complete solidification. After recrystallization from absolute alcohol, 2.35 g (70.8%) of colorless dihydrophysostigmoldimethylurethane hydrochloride with m.p. 188.5-189.0° was obtained.

3.140 mg substance: 6.685 mg CO_2; 1.960 mg H_2O. 3.360 mg substance: 0.318 ml N_2 (21°, 724 mm). 3.180 mg substance: 0.294 ml N_2 (23°, 732 mm). Found %: C 58.06; H 6.98; N 10.46, 10.27. $C_{13}H_{19}O_2N_2Cl$. Calculated %: C 57.65; H 7.08; N 10.35.

The base, isolated from the hydrochloride by treatment with cold, saturated sodium bicarbonate solution, was a thick, colorless oil which was readily soluble in the usual organic solvents

The picrate was prepared in alcoholic solution and recrystallized from alcohol; yellow needles with a m.p. of 123.5 - 124.0 were obtained (a mixture with picric acid melted at 78 - 80°).

The methiodide was obtained by treating an acetone solution of the base with methyl iodide. It crystallized from alcohol in the form of shiny needles with an m.p. of 206 - 207°.

3.010 mg substance: 4.960 mg CO_2; 1.550 mg H_2O. 3.035 mg substance: 4.990 mg CO_2; 1.435 mg H_2O. 5.540 mg substance: 0.377 ml N_2 (21°, 724 mm). 4.670 mg substance: 0.324 mg N_2 (25°, 728 mm). Found %: C 44.93, 44.83; H 5.76, 5.29; N 7.52, 7.61. $C_{14}H_{21}O_2N_2I$. Calculated %: C 44.67; H 5.63; N 7.45.

SUMMARY

The synthesis of the following analogs of the alkaloid eserine was effected: 1-methyl-5-hydroxyindoline methylurethane, and 1,3-dimethyl-5-hydroxyindoline (dihydrophysostigmol) methyl- and dimethylurethanes.

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REACTION OF HYDROGEN SULFIDE WITH ACETYLENIC AND VINYLACETYLENIC OXIDES

II. SYNTHESIS OF PHENYLTHIOPHENES

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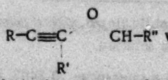


$R-C\equiv C-\underset{R'}{C}\overset{O}{\diagup\diagdown}CH-R''$

Recently, it was shown [1] that acetylenic oxides of the type R–C≡C–C(R')–O–CH–R" were converted into the corresponding homologs of thiophene by reaction with hydrogen sulfide in the presence of $Ba(OH)_2$. In order to extend the study of this reaction, it was considered desirable to determine whether or not oxides containing a phenyl-group as a substitutent for an acetylenic hydrogen would cyclize under these conditions. The following oxides were used for this study (see Table).

The synthesis of these oxides was effected from the chloroalcohols which were obtained by Iotsich's method The oxides are mobile, colorless liquids with a faint odor, which yellow upon storage in the air. They are not very stable thermally; upon heating at ordinary pressure, they rapidly polymerize, forming solid tar-like products which are insoluble in water, ether, and acetone. Upon vacuum distillation (2 - 10 mm), it is necessary to take small portions (20 - 25 g). Upon using larger amounts, not more than 60% can be distilled; the rest polymerizes. The process of polymerization, evidently, is accelerated by the polymerization products which are obtained during the process of the reaction since only a small amount of tarring occurs upon redistillation.

Oxide No.	Formula	Boiling point (in °)	n_D^{20}	d_4^{20}	MR_D	
					found	calculated
(I)	$C_6H_5-C\equiv C-\underbrace{C(CH_3)-CH_2}_{O}$ [2]	108 - 109 at 8 mm	1.5552	1.0278	49.21	4703
(II)	$C_6H_5-C\equiv C-\underbrace{(C_2H_5)-CH_2}_{O}$	111 - 112 at 4 mm	1.5520	1. 0112	54.33	5210
(III)	$C_6H_5-C\equiv C-\underbrace{C(CH_3)-CH}_{O}-CH_3$ [3]	121 - 122 at 8 mm	n_α^{17} 1.5435	d_4^{17} 1. 0220	53.2	51.2

A colorless liquid with a faint odor and with a b.p. of 123 - 124° at 5 mm; n_D^{20} 1.6299, d_4^{20} 1.1102; m.p. 16.5 - 17° corresponding to α-phenyl-β'-methylthiophene [4], was obtained by the reaction between hydrogen sulfide and 2-methyl-4-phenylepoxy-1,2-butyne-3 (I). A mixed melting point gave no depression.

The substance synthesized dissolves in strong sulfuric acid, gives a violet color with isatin sulfate, and forms a white precipitate with a m.p. of 177 - 179° with mercuric acetate.

α-Phenyl-β'-ethylthiophene was obtained by the reaction of 2-ethyl-4-phenylepoxy-1,2-butyne-3 (II) with hydrogen sulfide The product has a b.p. of 125 - 126° at 3 mm, n_D^{20} 1.6115, d_4^{20} 1.0779. It dissolves in strong, sulfuric acid, gives a violet color with isatin sulfate, and forms a precipitate with an m.p. of 194 - 196° with mercuric acetate.

α-Phenyl-α',β'-dimethylthiophene was formed under the same conditions by the reaction of hydrogen sulfide with 3-methyl-5-phenylepoxy-2,3-pentyne-4 (III). The substance synthesized was a yellowish liquid with a b.p. of 139 - 140° at 5 mm which crystallized in the receiver; m.p. 30 - 31°. It gives a grape color with isatin in strong sulfuric acid It forms a white precipitate with mercuric acetate, which decomposes at 240°.

The formation of phenylalkylthiophenes, therefore, has also been effected according to a previously suggested scheme [1].

EXPERIMENTAL

1. Preparation of 2-Ethyl-1-chloro-4-phenylbutyne-3-ol-2

80 g of 1-chlorobutanone-2 was added to ½ of a mole of phenylacetylenyl magnesium bromide in 400 ml

of absolute ether. The reaction mixture was left standing overnight and then decomposed with 30% acetic acid. The ether solution was dried with $MgSO_4$; the ether was removed and the remaining product vacuum distilled Two fractions were isolated: 1 - unreacted phenylacetylene, 14 g quantity, and 2 - a chloroalcohol with a b.p. of 140 - 141° at 5 mm, 68 g; n_D^{20} 1.5578, d_4^{20} 1.1067; MR_D 60.77. $C_{12}H_{13}OClF_3F$. Calculated: MR_D 58.41.

0.1298, 0.1524 g substance: 15.0, 17.6 ml CH_4 (15.5°, 764.3 mm). 0.4168, 0.2005 g substance: 0.2835, 0.1358 g AgCl. Found %: Act. H 0.499, 0.499; Cl 16.82, 16.75. Calculated %: Act. H 0.483; Cl 16.99.

2. Preparation of Oxide (II)

A colorless, mobile liquid with a faint odor was obtained by the treatment of the chloroalcohol with powdered KOH in ether solution.

0.1132, 0.1054 g substance: 0.3467, 0.3222 g CO_2; 0.0729, 0.0672 g H_2O. Found %: C 83.58, 83.42; H 7.21, 7.13. $C_{12}H_{12}O$. Calculated %: C 83.68; H 7.02.

3. Preparation of α-Phenyl-β'-methylthiophene

100 ml of water, 15 g of $Ba(OH)_2$, and 15 g of oxide (I) were placed into a round-bottomed flask with a mechanical stirrer. Hydrogen sulfide was passed into the reaction mixture for 2.5 hours at 70 - 80° (until the disappearance of the upper layer of the oxide). Then the calculated amount of acetic acid was added. The solution was extracted with ether, the ether layer separated, dried with $CaCl_2$, then with metallic sodium, and vacuum distilled. 9 g of α-phenyl-β'-methylthiophene (54.5%) was obtained.

Found: MR_D 55.84. $C_{11}H_{10}SF_3$. Calculated: MR_D 54.05.

0.3930, 0.3131 g substance: 0.5216, 0.4133 g $BaSO_4$. Found %: S 18.23, 18.13. $C_{11}H_{10}S$. Calculated %: S 18.40.

4. Preparation of α-Phenyl-β'-ethylthiophene

150 ml of water, 20 g of $Ba(OH)_2$, and 20 g of oxide (II) were used. The hydrogen sulfide was passed in for 4 hours at 60°. 14.5 g of a substance (66.3%) was isolated which was also redistilled over metallic sodium.

Found: MR_D 60.80 $C_{12}H_{12}SF_5$. Calculated: MR_D 58.80.

0.2918, 0.2792 g substance: 0.3637, 0.3511 g $BaSO_4$ Found %: S 17.12, 16.88. $C_{12}H_{12}S$. Calculated %: S 17.03.

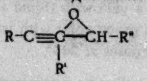
5. Preparation of α-Phenyl-α',β'-dimethylthiophene

150 ml of water, 20 g of $Ba(OH)_2$ and 25 g of oxide (III) were used. 17 g of phenyldimethylthiophene (62.9 %) was isolated after distillation of metallic sodium in vacuum.

0.2342, 0.1989 g substance: 0.2885, 2440 g $BaSO_4$. Found %: S 16.92, 16.85. $C_{12}H_{12}S$. Calculated %: S 17.03.

SUMMARY

1. α-Phenyl-β'-methylthiophene, α-phenyl-β'-ethylthiophene, and α-phenyl-α',β'-dimethylthiophene, previously unreported in the literature, were prepared by the reaction of hydrogen sulfide with the following oxides, respectively: 2-methyl-4-phenylepoxy-1,2-butyne-3, 2-ethyl-4-phenylepoxy-1,2-butyne-3, and 3-methyl-5-phenylepoxy-2,3-pentyne-4.

2. The formation of alkyl-, vinyl-, and phenylthiophenes from acetylenic and vinylacetylenic oxides of the type  $R{-}C{\equiv}C(R')\overset{O}{\frown}CH{-}R''$ by the action of hydrogen sulfide in the presence of $Ba(OH)_2$, appears to be a general reaction.

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Compounds, Leningrad State University

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* See Consultants Bureau English translation, page 1017.

** See Consultants Bureau English translation, page 1263.

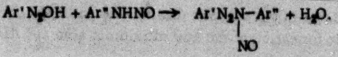
STRUCTURE AND TRANSFORMATIONS OF N-NITROTRIAZINES

I. DIARYL-N-NITROTRIAZINES

N. M. Baranchik, I. V. Grachev, and D. Z. Zavelsky

Among the various forms of diazo compounds, a neutral compound has been known for a long time [1], and has been erroneously regarded as an aryl nitrosoamine [2].

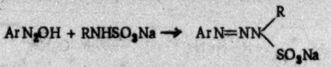
One of the authors [3] investigated this neutral compound by potentiometric titration and by other methods, and showed that it was N-nitrosotriazine (or diazonitrosoaminate). N-Nitrosotriazine is readily formed by mixing equimolecular solutions of a diazocompound and a nitrosoaminic acid.



$$Ar'N_2OH + Ar''NHNO \rightarrow Ar'N_2\underset{\displaystyle NO}{\underset{|}{N}}-Ar'' + H_2O. \qquad (1)$$

It is also formed by a spontaneous tautomeric transformation of diazodiazate or a nitrosoaminic acid. N-Nitrosotriazine is very unstable: it dissociates into the starting components readily in aqueous solution, and forms an azo compound by action of its active diazo form on the azo component; upon standing, it eliminates the nitroso group to form nitrous acid and diazoamino compounds, and is converted into other forms of diazo compounds by changes in the pH of the medium.

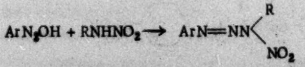
One of the authors [4] first obtained a compound of a new class, N-sulfatotriazine, by the condensation of an active diazo compound with sulfaminic acid and substituted sulfaminic acids:



$$ArN_2OH + RNHSO_3Na \rightarrow ArN{=}NN\begin{matrix} R \\ SO_3Na \end{matrix} \qquad (2)$$

It was found that triazine-N-sulfonic acids were unstable, and in a manner similar to N-nitrosotriazines, could decompose into the starting components or eliminate a sulfo group, the ease of either transformation depending upon the nature of the triazine radicals.

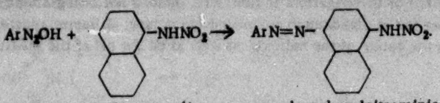
N-Nitrotriazine has not been known up to now. It could be supposed that N-nitrotriazine could be obtained by the condensation of active diazo compounds with nitroaminic acid in analogy to N-nitrosotriazines and N-sulfotriazines:



$$ArN_2OH + RNHNO_2 \rightarrow ArN{=}NN\begin{matrix} R \\ NO_2 \end{matrix} \qquad (3)$$

There are a large number of papers [5] on nitramines because of their resemblance to diazo compounds and application in several parts of industry. As is shown by G. S. Salyamon, I. V. Grachev, and B. A. Porai-Koshits [6], arylnitramines have the structure $ArNHNO_2$, and are true acids (arylnitraminic acids) which are close in strength to the carboxylic acids and are capable of giving salts of the structure $ArNMeNO_2$. By the action of acids, arylnitraminic acids are transformed into the corresponding nitroanilines by the transposition of a nitro group into the ring, and into the basic oxodiazohydrates $ArN{=}NOOH$.

However, in spite of the similarity of the arylnitraminic acids to diazo compounds, their reactions have not been studied sufficiently. It is only known that in certain cases this reaction leads to azo coupling in the para position to the nitramino groups [7]:



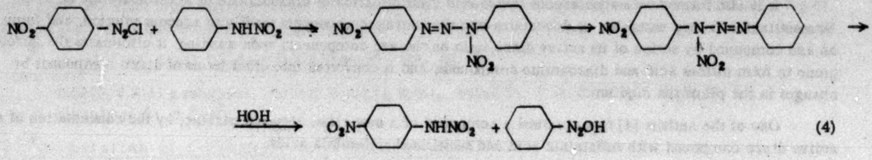
There are no other reactions between diazo compounds and arylnitraminic acids reported in the literature.

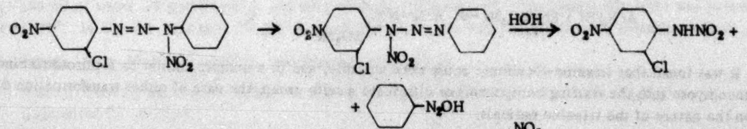
The aim of the present investigation was the preparation of diaryl-N-nitrotriazines by the reaction of active diazo compounds with arylnitraminic acids. The simplest of the nitramine class, phenylnitraminic acid, and the following diazo compounds were chosen for the reaction: p-nitrophenyl-, p-nitro-o-chlorophenyl-, and p-chloro-o-nitrophenyldiazonium. These diazo compounds were chosen because the presence of an electron-attracting group in their phenyl ring insures their diazo coupling activity with such weakly basic amines as phenylnitramines.

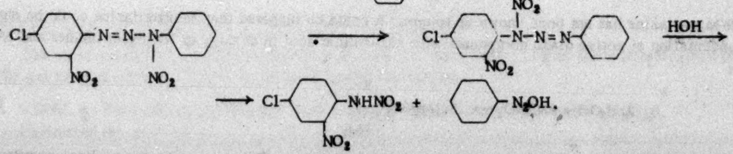
The reaction between phenylnitraminic acid and the diazo compounds, used in equimolecular amounts, was conducted in a weakly-acidic medium (pH 5 - 6). The isolated condensation product could not by crystallized and analyzed, because of its poor solubility in most solvents and its instability.

New nitraminic acids were isolated from the residue and from the solution, which contained aryl nuclei corresponding to the diazo compound participating in the reaction. In addition, the same new diazo compound was isolated in all cases, which had an aryl radical corresponding to the nitraminic acid participating in the reaction, namely, phenyldiazonium. p-Nitrophenyl-, p-nitro-o-chlorophenyl-, p-chloro-o-nitrophenylnitraminic acids isolated from the reaction mixtures were obtained in the form of crystalline products which were readily identified. Phenyldiazonium was determined by azo coupling in the form of phenyl azo-β-naphthol, as well as transformation into phenol, and then, into tribromophenol.

The appearance of the compounds isolated in the reaction products indicated the formation of diaryl-N-nitrotriazine which readily hydrolyzes with the formation of the new nitraminic acid and diazobenzene according to the following reactions:


(4)


(5)


(6)

The authors were first to observe the "transition" of the N-nitro group from the nitrogen to another nitrogen of the triazine which is combined with the nucleus having the electron-attracting substituents, as shown in equations (4), (5), and (6).

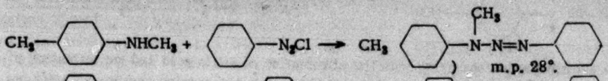
The asymmetric disubstituted triazine is subjected to tautomeric transformations [8] which are due to the movement of the imide hydrogen from one nitrogen of the triazine chain to the other, which is combined with the nucleus having the electron attracting substituent:

$$R'-N{=}N-NH-R'' \rightarrow R'-NH-N{=}N-R''.$$

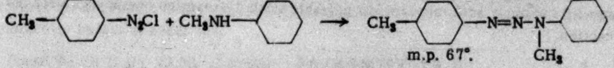
In spite of the large number of investigations in this field, there is not a single idea relative to the mechanism of the tautomeric transformation of diazoamino compounds up to now. It seems apparent that the position of the imide hydrogen depends on the nature of the radicals, as well as on the pH of the medium in which the triazine is found [9].

A study of the metallic salts of the triazines [10] showed that these salts can be represented as internal complexes in which the triazine system is the chelating part of the molecule. On the basis of the study of the molecular weight of the triazines [11], it was shown that the triazine molecules are associated in solution, and possibly, in solid state. Two forms of association are suggested, linear and cyclic.

If the imide hydrogen in the diazoamino compound is substituted by an alkyl radical, it loses its ability for tautomeric transformation. Thus, a compound with a single composition with m.p. 28° was obtained from N-methyltoluidine and diazobenzene [12], another with m.p. 67° from N-methylaniline and diazotoluene. Both of these isomeric compounds showed no tendency to tautomeric changes:



(7)

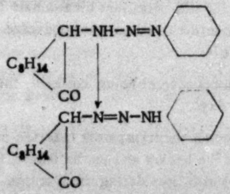


(8)

Analogous isomeric compounds with a fixed ethyl group which are incapable of tautomeric transformation [13] can be cited as another example: one compound obtained by the coupling of m-nitrobenzene with ethyl-p-nitroaniline; another, by the coupling of p-nitrodiazobenzene with m-nitroethylaniline. However, if the diazoamino compounds themselves are alkylated, then a mixture of both compounds is obtained.

It must be mentioned that the methyl and sulfo groups in arylmethylsulfotriazines occupy strictly fixed definite positions, and the compounds do not possess tautomeric properties [4].

However, there is one paper [14] in which the migration of an acyl radical is reported. Thus, camphorylphenyltriazine was obtained by the coupling of aminocamphor with diazobenzene, which was assigned structure (b) on the basis of the investigation of the decomposition products, even though structure (a) should have been assigned to it according to the method of preparing it.

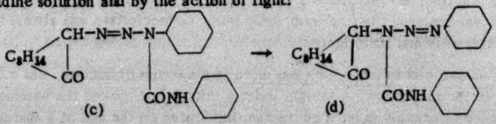


(a)

(b)

(9)

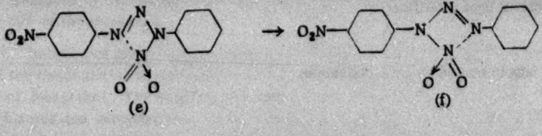
(b) forms the urea derivative (c) by treatment with phenyl isocyanate, which is transformed into compound (d) by heating in pyridine solution and by the action of light:



(10)

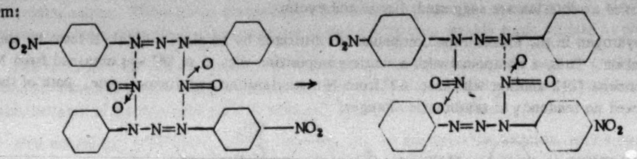
The movement of the phenylcarbamide group was detected by an investigation of the decomposition products and the sharply different optical properties of compounds (c) and (d).

The N-nitrotriazine obtained must have structure (e) according to the method of preparation. It can be supposed that the triazine undergoes an intramolecular redistribution of the electronic density by the action of the electron attracting group of the aromatic radical as a result of which the nitro group moves to the other nitrogen. A new triazine structure (f) is formed to which the decomposition products correspond.



(11)

With the presence of association of the molecules of N-nitrotriazines, the movement of the nitro group, viewed as an intermolecular interaction, becomes more probable. The scheme of such a movement explaining the appearance of compounds indicating the transposition of the nitro group in the reaction products can be shown simply in the following form:


(12)

Hydrolysis of the N-nitrotriazine occurring with the elimination of nitric acid and the formation of a new N-nitrotriazine by nitration with the nitric acid, appears less probable, since diazoamino compounds were not detected in the products of the reaction.

EXPERIMENTAL

1. Condensation of phenylnitraminic acid with diazo compounds. A solution consisting of 1.60 g of the sodium salt of phenylnitraminic acid (0.01 mole), 25 ml of water, and 25 - 40 ml of a concentrated acetate buffer solution having a pH of 6 and containing 125 g of potassium acetate and 30 ml of glacial acetic acid in 200 ml of solution, was charged into a round-bottomed beaker fitted with a stirrer. The nitraminic acid was synthesized by the oxidation of the nitrosoaminate of the corresponding diazocompound in alkaline medium [15]. * The reaction beaker was cooled externally with ice so that the temperature of the solution was about 5°, and a solution of the diazo compound (0.01 mole) was added with rapid stirring over a 15-minute period. The diazo compound was prepared by the diazotization of 0.01 mole of the corresponding amine [16], freed from excess nitrous acid, and were used, in the form of hydrochloric acid solutions containing 0.01 mole of the diazo compound and a 2-fold excess of hydrochloric acid, for the reaction.

In order to neutralize the acid introduced with the diazo compound solution (0.02 mole) and freed during condensation process (0.01 mole), it was necessary to add potassium bicarbonate or acetate. The reaction medium varied from pH 4.8 - pH 5.8. The control of the reaction medium was conducted on removed samples with a pH meter of the system GIPKh with glass electrodes [17].

The condensation was virtually complete after several hours; however, the diazo compound, giving a color reaction with R-salt, remained in solution for 2 - 3 days.

Soon after the addition of the diazo compound, the transparent reaction mixture became cloudy, and dark drops of a tarry substance appeared on the walls of the beaker and on the stirrer, the amount of which rapidly increased. This tar was partially converted into brownish flocs during the reaction, which settled to the bottom, or were found on the surface of the solution.

At the end of the reaction, the solution was filtered and the precipitate was washed with a large amount of water on the filter. As it was observed that the wash water from the precipitate was always rather green-yellow in color, it was collected separately and investigated.

The filtered and washed precipitate which was dried in a vacuum desiccator, was a dark-brown powder with darker inclusions visible to the naked eye. A sample under a microscope showed the heterogenous composition of the residue, and the absence of crystals in it. The residue, introduced on the end of a spatula into the flame of a burner, first melted with swelling, and then burst, leaving a carbonized mass. It was found to be partially soluble in ethyl alcohol, benzene, and chloroform, with the solutions being red or red-brown. Bubbles of a gas were evolved upon the solution of the crude residue in alcohol. The residue dissolved almost completely in acetone, coloring the solution brown. However, attempts to isolate the substance from solution in crystalline state were unsuccessful; upon cooling a saturated solution or upon diluting it with water, flocs tarry in character appeared.

The residue was treated in the cold with 0.5 N alkali, and a dark red solution was obtained. Solution was not complete even after prolonged treatment with a large amount of alkali. These alkaline solutions, however, also formed amorphous brown precipitates upon acidification.

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* The method was refined and supplemented by G. S. Salyamon

2. Isolation of the substance from the aqueous solution. The aqueous solution (filtrate, aqueous extract of the residue) which had a pH 6-7, was shaken with ether to remove the side products and then acidified with 10% hydrochloric acid to pH 3. The acidified solution was again extracted with ether, and the substance which colored the water solution was completely transposed into the ether layer. The ether was removed by evaporation at room temperature, and the crystals which formed were recrystallized many times from a mixture of alcohol and water.

3. Identification of the substances isolated from the aqueous solution. a) Substance obtained by the condensation of p-nitrophenyldiazonium with phenylnitraminic acid The compound obtained was a light yellow crystalline substance with m.p. 110-111° which was poorly soluble in water and readily soluble in aqueous alkalies, alcohol, and ether. This compound burned explosively and gave a Liebermann reaction with a color characteristic for nitraminic acids. According to potentiometric titration data, it was a rather strong acid and had a molecular weight of about 184.

Found %: N 22.95, 23.00. $C_6H_5O_4N_3$. Calculated %: N 22.95.

According to all its properties, the compound obtained was identical with p-nitrophenylnitraminic acid which, according to literature data [18a] has an m.p. 110-111°. The identity of the compound isolated with p-nitrophenylnitraminic acid was proved by the absence of a depression in a mixed melting point with specially synthesized p-nitrophenylnitraminic acid. The latter was synthesized by the oxidation of the nitrosoaminate of p-nitrophenylhydrazone in alkaline medium; its m.p. was 111-112°. The mixed melting point was 111-112°.

b) Substance obtained by the condensation of p-chloroo-nitrophenyldiazonium with phenylnitraminic acid. The compound obtained was a light yellow crystalline substance with m.p. 107-108° which was poorly soluble in water and readily soluble in aqueous alkalies, alcohol, and ether. This compound burned explosively and gave a Liebermann reaction with a color characteristic for nitramines According to potentiometric titration data, the compound was a rather strong acid and had a molecular weight of about 217.

Found %: N 19.55, 19.62. $C_6H_4O_4N_3Cl$. Calculated %: N 19.31.

The identity of the compound obtained with p-chloro-o-nitrophenylnitraminic acid which has an m.p. 107-108° according to the literature data [18b], was proved by the absence of a depression in a mixed melting point with the specially synthesized nitraminic acid. The latter was synthesized by the oxidation of the corresponding nitrosoaminate in alkaline medium; its m.p. was 108-109°. The mixed melting point was 108-109°.

c) Substance obtained by the condensation of p-nitro-o-chlorophenyldiazonium with phenylnitraminic acid. The compound obtained was a light yellow crystalline substance with m.p. 92-93° which was poorly soluble in water and readily soluble in aqueous alkalies, alcohol and ether. This compound burned explosively and gave a Liebermann reaction with a color characteristic for nitramines. Potentiometric titration data were the same as for the previous compound.

Found %: N 19.62, 19.52. $C_6H_4O_4N_3Cl$. Calculated %: N 19.31.

According to all of its properties, the compound obtained was identical with p-nitro-o-chlorophenylnitraminic acid, which is unreported in the literature, and was synthesized by the authors by the oxidation of the nitrosoaminate of the corresponding diazo compound in alkaline medium; m.p. 93-94°. The identity of the compounds obtained during the condensation reaction and the synthesized nitraminic acid, was proved by the mixed melting point, 93-94°.

4. Isolation of phenol. Phenol was isolated from the reaction mixture obtained by the condensation of the diazonium with phenylnitraminic acid. The reaction was conducted for 1-2 hours, and was stopped when the appearance of some of the tarry substance was first noticed in the reaction vessel. The entire reaction mixture including the tar, was heated almost to 100° in a period of several minutes; it was then steam distilled, after filtration and neutralization with 10% sodium hydroxide solution from pH 4-5 to pH 8. Phenol was detected in the condensate, approximately 300 ml, which was isolated in the usual manner in the form of tribromophenol and was identified by comparison with specially synthesized tribromophenol. The yield of phenol was approximately 30% of the theoretical.

5. Isolation of phenylazo-β-naphthol. The filtrate after the separation of the residue obtained as a result of the condensation of p-chloro-o-nitrodiazobenzene, was subjected to diazo coupling with an alkaline solution of β-naphthol. The coupling was conducted in a weakly acidic medium (pH 5-6). The precipitated dye was filtered and recrystallized many times from a mixture of alcohol and water. According to its melting

point, the isolated dye was identical with phenylazo-β-naphthol having an m.p. 130-131° [18c]; the melting point of the analogous compounds having a nitro, or nitro and chloro group, in the phenyl radical was considerably higher; namely, from 240-250°. Even though the isolated dye could not be purified from a difficultly separable impurity, and its melting point was somewhat lower than that of the specially synthesized phenylazo-β-naphthol, nevertheless, according to a mixed melting point, it was phenylazo-β-naphthol.

SUMMARY

1. The reaction between the diazo compounds, p-nitrodiazobenzene, p-nitro-o-chlorodiazobenzene. and p-chloro-o-nitrodiazobenzene and phenylnitraminic acid was studied. and the unstable diaryl-N-nitrotriazines, identified by their decomposition products, were detected for the first time.

2. The decomposition products of the diaryl-N-nitrotriazines were diazobenzene and a nitraminic acid with a nucleus corresponding to the diazo compound participating in the reaction, which indicates the transfer of the nitro group from one nitrogen of the triazine to the other, which was connnected to the more negative radical.

3. The possible mechanism, which was the not-previously-encountered transfer of a nitro group in a N-nitrotriazine from one nitrogen to another. was discussed.

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PREPARATION, PROPERTIES, AND STRUCTURE OF COMENIC ACID
(5-HYDROXY-γ-PYRONE-2-CARBOXYLIC ACID)

G. A. Garkusha

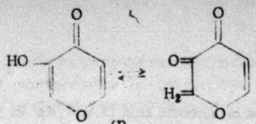
Comenic acid is usually obtained by the decarboxylation of meconic acid [1, 2, 3, 4]. As was previously reported by the authors [6], its yield was 80% based upon purified dry meconic acid, and the comenic acid obtained, was not sufficiently pure. This depended upon the method of isolating meconic acid, the nature of which was related to the processing of the opium industry wastes, meconates, with dilute hydrochloric acid followed by purification by means of the potassium [7], or ammonium salts [3]. Mennel [8] employed dilute hydrochloric acid. Each of these methods has one or another drawback.

Since all of the methods for the isolation of meconic acid are rather laborious, the preparation of comenic acid directly from the meconates was of great interest. It was found that this could be accomplished by decarboxylating the meconates themselves. However, such a method was found to be applicable only for samples containing large amounts of meconic acids. Its application to the usual samples of meconates led to a strong tarring of the reaction mass, which in itself complicated the isolation of comenic acid and decreased its yield considerably. The starting products for the preparation of comenic acid were the usual samples and those from which meconic acid could not be isolated by known methods. It was found that, by using an initial treatment with HCl diluted 3:1, 2:1, or 1:1 (second figure is water) in the cold, comenic acid of a high degree of purity could be obtained from such samples of meconates, as well as from meconic acid. This method differs from the known methods of preparation of comenic acid in that it gives a product of a high degree of purity, as was determined by a determination of its melting point and the temperature of its decarboxylation.

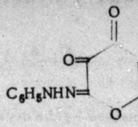
The structure of comenic acid as 5-hydroxy-γ-pyrone-2-carboxylic acid was proved by the following facts. The acid is a derivative of 3-hydroxy-γ-pyrone, as this hydroxypyrone forms upon its decarboxylation [6, 9, 10]. It is also obtained by the decarboxylation of meconic acid, which is also a derivative of 3-hydroxy-γ-pyrone (Thoms and Pietrulla [11]). Peratoner and Leone [12] showed that a small amount of comenic acid was formed on heating the sodium salt of 3-hydroxy-γ-pyrone with carbon dioxide. A series of authors [3, 8, 13, 14, 15] showed that bromocomenic acid was obtained by the bromination of comenic or meconic acid, (1 mole bromine), as well as 6-iodocomenic acid [6] by their iodination. 6,6-Dibromocomenic acid was obtained by the action of 1 mole of bromine on 6-bromocomenic acid, or 2 moles of bromine on meconic acid. The structure of this acid as 3,6-dibromo-5-hydroxy-γ-pyrone-2-carboxylic acid is not very probable, since it readily eliminates a bromine with the formation of 6-bromocomenic acid [8] when heated to 105°, or upon reduction with zinc or tin and hydrochloric acid. Its structure as 6,6-dibromocomenic acid is explained by the appearance of tautomers [16]. The formation of an α-diketone group was proved by the preparation of a quinoxaline derivative, as well as the corresponding hydrazone. It is true that other authors could not duplicate these reactions.

The hydrolysis of 6-bromocomenic acid leads to the preparation of 6-hydroxycomenic acid (5,6-dihydroxy-γ-pyrone-2-carboxylic acid). A series of authors [5, 13, 15] showed that this hydrolysis proceeds smoothly. The same acid was obtained by the hydrolysis of 6-iodocomenic acid [6].

The transformation of comenic acid into comenamic acid, and the preparation of dihydroxypyridine from it, serves as proof of the structure of 3-hydroxy-γ-pyrone and comenic acid [13, 17, 21, 22]. If the former is transformed into 3, 4- or 4, 5-dihydroxypyridine, then the position of the hydroxyl group in the hydroxypyrone only is demonstrated, but not in comenic or meconic acids, since the cited dihydroxypyridines can be formed from these acids if the hydroxyl group is in the ortho, or in the para position. For this reason, the attempt of Belonson [18] to prove the structure of comenic acid as 3-hydroxy-γ-pyrone-2-carboxylic acid by the fact that he obtained 3,4-dihydroxypyridine from it, cannot stand up under criticism. This fact resulted in the erroneous conclusion on the structure of comenamic acid as 3,4-dihydroxypyridine-2-carboxylic acid, as well as the erroneous interpretation in the communication of Peratoner and Tamburello [19] who showed that the hydroxyl group was found in the para position in comenamic and comenic acids. The latter is confirmed in the communication of Jabuta [20], who obtained 4,5-dihydroxy-2-methylpyridine from comenamic acid and kojic acid. It was also shown that 5-hydroxy-2-methyl-γ-pyrone obtained by the reduction of kojic acid, reacted with phenyldiazonium acetate to form "red crystals" of the azo compound(?!)*. Apparently, its phenylhydrazone (II) was obtained by Peratoner and Carapelle [24] during an attempt to prepare the azo compound from 3-hydroxy-γ-pyrone, which is only possible with occurrence of a keto-enol rearrangement (I). The quinoxaline derivative (III) of this phenylhydrazone (II) was obtained by reaction with o-phenylenediamine, and γ-pyrone trihydrazone (IV) by the condensation of (II) with 2 moles of phenylhydrazine.



(I)



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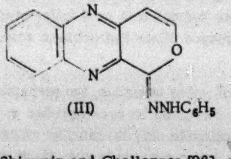
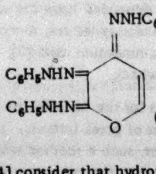
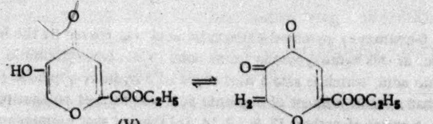


(III)

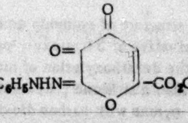


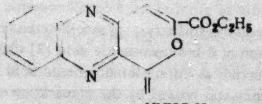
(IV)

Since Shimmin and Challenger [26], quoting from [24] consider that hydroxypyrone phenylhydrazone was an authentically reported compound, we decided to test this premise. It was found that the reaction proceeded smoothly, but that the isolation of the hydrazone was hindered by its easy oxidizability especially in the moist state. By changing the reaction conditions and the procedure of isolating its products, 3-hydroxy-γ-pyrone sulfonamidophenylhydrazone was obtained. Later, an attempt was made to prepare comenic acid phenylhydrazone based on the preparation of ethyl comenate phenylhydrazone, using phenyldiazonium acetate. This attempt was unsuccessful. For this reason the quinoxaline derivative (VIII) was obtained from hydrazone (VII):



(V) (VI)





Undoubtedly, the formation of hydrazone (VII) is possible only if it is assumed that the structure of comenic acid is 5-hydroxy-γ-pyrone-2 carboxylic acid, and therefore that of its ester (V). The formation of the hydrazone cannot occur with any other position of the hydroxyl group in these compounds. By using phenyldiazonium chloride, it was possible to obtain comenic acid phenylhydrazone, as well as to isolate its acid sodium salt. The neutral salt was found to be unstable.

Finally, an indirect proof of the formation of these hydrazones of hydroxypyrone, comenic acid, and its ester, which is assured by the occurrence of tautomerism, is the absence of the latter in maltol, 3-hydroxy-2-methyl-γ-pyrone, which does not react with phenyldiazonium, sulfonyl chloride, or amylnitrite, and by the fact that its halogen derivative has not been obtained. The structure of maltol as 3-hydroxymethyl-γ-pyrone was proved by its synthesis from 3-hydroxy-γ-pyrone [25].

Therefore, the ability of comenic acid and its ethyl ester to form hydrazones agrees with its structure as 5-hydroxy-γ-pyrone-2-carboxylic acid, and not 3-hydroxy-γ-pyrone-2-carboxylic acid.

EXPERIMENTAL

1. Preparation of comenic acid. 100 g of pulverized meconates was added in portions with stirring at a temperature not higher than +10° to 140 ml of hydrochloric acid (sp. gr. 1.19) and 70 ml of water. After stirring for 0.5 hours, the residue was filtered and washed with ice water. 80 g of this residue was added, at 80-85° within the reaction mixture, to 150 ml of hot dilute hydrochloric acid (1:1). The decarboxylation was over in 1 hour,

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* True, the authors did not characterize this compound.

and 80 ml of a 10% sodium chloride (C.P.) solution was added at 70°. The precipitate which formed after twenty-four hours was filtered and washed with ice water and alcohol. The weight of the air-dried residue was 40 g; that dried at 100 - 110°, 30 g.

40 g of the air-dried comenic acid was purified by mixing it with 560 ml of water and adding $NaHCO_3$ in small portions (to 20 g) until the reaction was just acid (brown on Congo). The mixture was then heated to 70 - 75° until complete solution. The hot solution was filtered with carbon, and 150 g of sodium chloride was added to the filtrate, with stirring. The precipitated white crystals of the acid sodium salt were filtered and washed with the mother liquor and with alcohol. 45 g of the precipitate was mixed with an equal amount of water and 90 ml of hydrochloric acid, and then 45 ml of water was added. The comenic acid was filtered and washed with ice water and alcohol. The chlorides were removed by mixing the residue with water in a ratio of 1:2, followed by heating and cooling to 0°, and processing in the above manner. Dried at 120°, the snow-white crystals weighed 20 g; m.p. 273 - 274° (with tarring); 274 - 275° in a sealed capillary. Upon heating a layer of crystals on a cover glass in a Maken block melting point apparatus, they decarboxylated without leaving a residue and without changing color at 225 - 230° (the temperature was measured at the usual position of the thermometer in the apparatus). Aqueous and alcoholic solutions of ferric chloride were colored blood-red by the addition of the crystals.

2. Preparation of 3-hydroxy-γ-pyrone phenylhydrazone. 5.5 g of anhydrous sodium acetate was added to a diazo solution prepared from 1.9 g of sodium nitrite, 2.4 g of aniline, 6 ml of HCl, and 12 ml water with ice. 2.8 g of 3-hydroxy-γ-pyrone in 28 ml of water acidified with 1.2 ml of acetic acid was added at 0°. After 1 hour, a 1% hydrochloric acid solution was added at +5° to a violet reaction (Congo). The raspberry red precipitate was filtered and washed with ice water acidified with HCl (blue on Congo), the precipitate being kept covered, and then with water and ice. The blood-red crystals obtained were air dried. The yield was 5 g. The crystals were insoluble in petroleum ether and ethyl ether, and poorly soluble in xylene. Recrystallized from hot xylene, they had a broad melting point about 170° (176° according to Carapelle) with a change of color; at 190° the viscous mass carbonized.

When 1 g of crystals mixed with 5 ml of water acidified with HCl (blue on Congo), was treated with sulfur dioxide for 5 hours, they dissolved completely. Twenty-four hours later, yellow brown crystals insoluble in water, chloroform, and ether, and soluble in alcohol and acetone, came out.

3. Preparation of 3-hydroxy-γ-pyrone-p-sulfamidophenylhydrazone. 3.5 ml of HCl (sp. gr. 1.19) and a solution of 0.85 g of sodium nitrite in 3 ml of water was added in 20 minutes at 0° to a mixture of 2.16 g of sulfanilamide and 12 ml of water. 3.5 ml of glacial acetic acid and 7.5 ml of 30% sodium acetate solution were added at −3° to the diazo solution (violet color on Congo). To the phenyldiazonium acetate at −3° was added a solution of 1.4 g of 3-hydroxy-γ-pyrone in 20 ml of water with 3 ml of glacial acetic acid, and 3.5 ml of a 30% sodium acetate solution (red color on Litmus). A sample on filter paper was used to test the end of the reaction. The precipitate was filtered rapidly, washed with water and ice (without uncovering it) for 30 minutes, acidified water and ice, and once more with water and ice. The residue, dried in the air, and then at 100°, weighed 1.8 g, which corresponded to 51% of the theoretical yield: bright red crystals with m.p. 260 - 265°, with the color of the melt changing to brown. It was insoluble in benzene, xylene, chloroform, and ether, difficultly soluble in alcohol; upon heating with acetone, solution occurred and a white precipitate formed.

0.7005 g substance: 0.5805 g $BaSO_4$. 0.3555 g substance: 0.409 ml N_2 (21°, 740 mm) (according to Dumas). 0.2920 g substance: 0.341 ml N_2 (20.5°, 741 mm) (with CuO). Found %: S 11.38; N 13.01, 13.24. $C_{11}H_{11}O_5N_3S$. Calculated %: S 10.8; N 14.25.

4. Preparation of ethyl comenate p-sulfamidophenylhydrazone. 17.2 g of sulfanilamide was added in portions with stirring at 0° to a mixture of 28 ml of HCl (sp. gr. 1.19), 96 ml of water, and 30 g of ice After solution of most of the sulfanilamide, 30 g more of ice and a solution of sodium nitrite (7 g in 25 ml of water) was added, with continuous stirring until complete solution of the sulfanilamide, with the addition of 40 g more of ice. A solution of 18.5 g of ethyl comenate in 180 ml of 80% acetic acid was added to the diazo solution at +3°, and 100 ml of 30% sodium acetate, steadily, but not allowing the reaction to be violent, or the temperature to rise above +5°. A dark red precipitate of hydrazone was formed by the addition of 100 g of sodium chloride and acidification with dilute HCl (1:1) while the reaction mixture was cooled to −10°. The completion of precipitation was tested with a sample on filter paper. The precipitate was filtered immediately, washed with a saturated sodium chloride solution with ice (keeping the precipitate covered), and then with water and ice. Air dried, and then at 90 - 100° the dark red precipitate weighed 27.5 g which corresponded to 75% of the theoretical yield. The substance was insoluble in benzene, toluene, ether and petroleum ether: it was slightly soluble in chloroform, and gave a red solution;

it was slightly soluble in ethyl acetate, alcohol (absolute), and methanol (solutions colored yellow); it was readily soluble in pyridine and nitrobenzene (solutions colored yellow). Solution occurred upon heating with acetone, and a white precipitate formed. The crystals dissolved in nitrobenzene and precipiated with benzene, had a dark red color; dried, a raspberry. M.p. 173-175° (with carbonization).

0,2970 g substance: 0.4970 g CO_2; 1.010 g H_2O. 0,3380 g substance: 0,385 ml N_2 (23°, 734.5 mm). 0,3760 g substance: 0,325 ml N_2 (22°, 73.8 mm). 0,2880 g substance: 0.256 ml N_2 (23°, 735 mm) (according to Dumas). 0,6140 g substance: 0.3910 g $BaSO_4$. 0.7380 g substance: 0.4770 g $BaSO_4$. Found %: C 45.64; H 3.81; N 9.4, 9.72, 9.92; S 8.74, 8.87. $C_{14}H_{13}O_7N_3S$. Calculated %: C 45.8; H 3.54; N 11.7, S 8.73.

5. Preparation of the quinoxaline derivative. 0.6 g of ethyl comenate p-sulfamidophenylhydrazone was dissolved in 4 ml of pyridine, acidified with 1 ml of glacial acetic acid, and mixed with a solution of 0.2 g of o-phenylenediamine in 2 ml of glacial acetic acid. After filtrationof the solution which was heated to 80°, and cooling to 30°, a purple-red precipitate formed which was filtered and washed with methanol, ether, and benzene, and dried at 105°. 0.6 g of crystals were recrystallized from a mixture of pyridine and acetic acid. M.p. 290-295° (with carbonization).

0.4420 g substance: 0.599 ml N_2 (24°, 728 mm). 0.2170 g substance: 0.299 ml N_2 (23°, 728 mm). 0.5770 g substance: 0.3195 g $BaSO_4$. Found %: N 14.92, 15.22; S 7.6. $C_{20}H_{17}O_5N_5S$. Calculated %: N 15.95; S 7.3.

6. Preparation of comenic (5-hydroxy-γ-pyrone-2-carboxylic) acid phenylhydrazone. A solution of 2.6 g of sodium nitrite in 10.5 ml of water was added at 1-3° to a solution prepared from 2.8 g of aniline and 10.5 ml of HCl (sp. gr. 1.19), diluted with 26 ml of water. At the same time, 4.7 g of comenic acid was dissolved at 60-70° in 140 ml of water with the addition of 2.3 g of anhydrous potassium carbonate. This solution was cooled to +15° (the salt precipitated upon rapid cooling) and added to the diazo-solution. Then 60 g of sodium chloride was added, and the reaction mass was cooled to −5°. Dilute HCl (1 : 1) was added in portions, testing the completion of precipitation with a sample on filter paper. The back precipitate was filtered through a cloth filter (leaving it under the liquid) and washed, first with a saturated sodium chloride solution acidified with HCl (litmus) with pieces of ice, and then with ice water, and ether. Weight of the moist residue was 5.6 g. Weight in air-dried state, 3.5 g (black color with a red-violet sheen).

This 3.5 g of precipitate was mixed with 50 ml of water, and about 4.5 ml of 20% Na_2CO_3 was added to a neutral reaction (yellow on bromothymol blue). The solution obtained was filtered with carbon, and 12 g of sodium nitrate was added to the filtrate with stirring until it dissolved. The hydrazone salt was precipitated with 100 ml of alcohol, filtered, and washed with a mixture of alcohol and ether (1 : 1). The sodium nitrate was washed out by one or two mixings with 70% alcohol; the completion of the washings was tested with diphenylamine. The weight of the air-dried precipitate was 2.5 g. The dried black crystals (red-violet sheen)had an m.p. of 195-198° (with tarring). The substance was insoluble in chloroform, benzene, ether, and ethyl acetate; it was slightly soluble in cold water, and to an extent of 1:40 in water heated to 45°. Upon heating with an excess of water to 60-70°, decomposition occurred continuing for several hours. The hydrazone was considerably more soluble in acetic acid and alcohol. Its acid sodium salt was red-violet, the neutral salt, orange. A solution of the neutral sodium salt decomposed completely upon standing for twenty-four hours at room temperature. The acid sodium salt of the hydrazone was more stable. It dissolved to an extent of 1:10 in water at 20°, and 1:5, at 45°. It was insoluble in alcohol, acetone, and ether. The acid sodium salt, precipitated from an aqueous solution with alcohol, did not have a sharp melting point: at 240°, the crystals became dark brown, at 250° they shrank and became grey, at 270° they blackened and, finally, at 300° and higher, the mass puffed up.

Because the red-violet solution of the acid sodium salt of the hydrazone was different from the orange solution of the neutral salt, it was possible to titrate it without an indicator (a recrystallized substance with m.p. 195-198° was used).

0.2800 g substance: 0.5650 g CO_2; 0.08250 g H_2O. 0.5260 g substance in 5.4 ml of water: 20.0 ml 0.1 N HCl. 0.6820 g substance in 7.0 ml water: 26.0 ml 0.1 N HCl. Found %: C 55.01; H 3.28; M 264, 262. $C_{12}H_8O_5N_2$. Calculated %: C 55.3; H 3.08; M 260.

SUMMARY

1. A method for the preparation of comenic acid directly from the meconates is given.

2. The following compounds, unreported in the literature up to now, were obtained: 3-hydroxy-γ-pyrone, ethyl comenate p-sulfamidophenylhydrazone, and its quinoxaline derivative, and comenic acid phenylhydrazone.

3. The structure of comenic acid was proved to be 5-hydroxy-γ-pyrone-2-carboxylic acid by the obtaining of the above hydrazones.

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* See Consultants Bureau Translation, page 127.

[illegible] 42. The following compounds, prepared in the [illegible] were obtained: [illegible] and [illegible] hydrazones.

4. The structure of [illegible] acid [illegible] of the above hydrazones.

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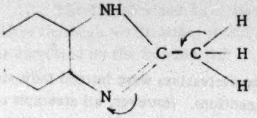
REACTIVITY OF CERTAIN DERIVATIVES OF 2-METHYLBENZIMIDAZOLE

I. REACTIONS OF THE METHYL GROUP HYDROGENS

B. A. Porai-Koshits and Kh. L. Muravich

During the many years of investigating problems of the reactivity of organic compounds, A. E. Porai-Koshits studied especially thoroughly substances possessing active hydrogen atoms in methyl and methylene. The activity of the hydrogen atoms enables these substances to participate in condensation reactions with aldehydes, nitroso compounds, and diazo compounds. The relationship to these compounds characterizes the degree of reactivity of the hydrogen atoms of the methyl or methylene groups; the most active are those compounds which can condense not only with aldehydes and nitroso compounds, but can also participate in coupling reactions with diazo compounds. A. E. Porai-Koshits' investigations to determine the relation of the structure of substances possessing active hydrogen atoms in methyl and methylene groups, made possible the following summary in the form of a rule: if the methyl or methylene group is found in conjugation with the hetero atom, then its hydrogen atoms acquire an increased reactivity [1]. Therefore, the reactivity of the H atoms in these substances is due to the ability of the hetero atom to shift electrons.

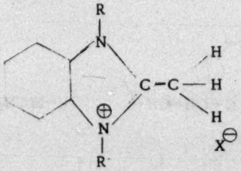


(I)

2-Methylbenzimidazole (I) can be assigned to those compounds possessing reactive hydrogen atoms on the basis of A. E. Porai-Koshits' rule, and it is able to participate in condensation reactions with aldehydes, isatin, phenanthrenequinone, and phthalic anhydride [2].

However, the reactivity of the hydrogen atoms of these substances is comparatively small, and the condensation reactions proceed only under forcing conditions. 2-Methylbenzimidazole is almost unable to react with nitroso- and diazo compounds [3]. The reason for the small reactivity of these compounds was seen by A. E. Porai-Koshits in the fact that the nitrogen of the group $-C=\overline{N}-$, possessing an unshared pair of electrons, does not polarize the carbon-hydrogen bond strongly enough; on the other hand, this small polarization is weakened by the presence of an imino group whose unshared pair of electrons compensates the partial positive charge on the carbon atom in position 2.

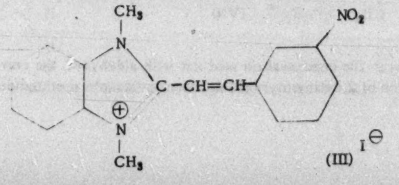
It appeared possible to verify experimentally this explanation by synthesizing derivatives of 2-methylbenzimidazole in which the effect of the unshared pair of electrons on the nitrogen atom was eliminated, and to study the reactivity of the methyl groups of these compounds. The simplest method for blocking the unshared electron pair of one of the nitrogen atoms appeared to be the conversion of this compound into the quaternary derivative (II). The present investigation started with the synthesis of such a compound and the study of its properties. Initially, the methiodide derivative of 1,2-dimethylbenzimidazole was synthesized by the methylation of 2-methylbenzimidazole. The latter was obtained by heating o-phenylene diamine with acetic acid in a sealed tube.



(II)

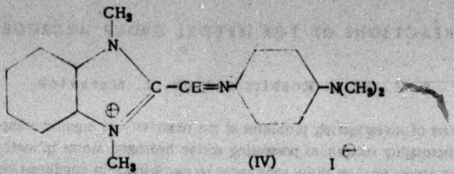
The quaternary compound obtained was found to be capable of reacting with m-nitrobenzaldehyde with a much greater ease than 2-methylbenzimidazole. The formation of the condensation product occurs even when the starting substances are boiled in alcoholic medium in the presence of piperidine.

The reaction product, light yellow crystals, is 3-methyl-2-m-nitrostyrylbenzimidazole methiodide (III).



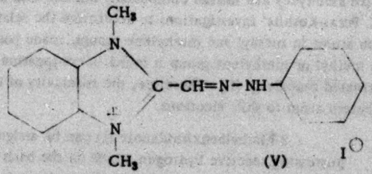
(III)

The condensation reaction with p-nitrosodimethylaniline proceeds under these conditions with the formation of violet crystals of the azomethine (IV). The latter possesses the characteristic properties of azomethines; ie., it can be hydrolyzed upon heating with dilute hydrochloric acid. The aldehyde formed as the result of the



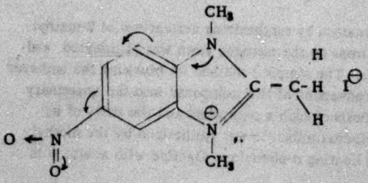
(IV)

hydrolysis was converted into 3-methylbenzimidazol-2-aldehyde p-nitrophenylhydrazone methiodide (V) by reaction with p-nitrophenylhydrazone.



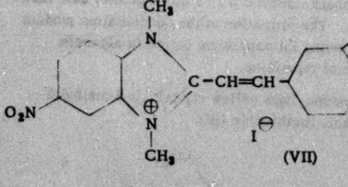
(V)

The ease with which the condensation products with aldehydes and nitro derivatives were formed indicated that the investigated compound was capable of participating in azo coupling reactions. However, all attempts to obtain the azo dye by coupling the methiodide derivative with diazo compounds from p-nitroaniline were unsuccessful. The reason for this behavior, evidently, is the presence of the second hetero atom. It is possible to assume that the unshared pair of electrons of the latter partially neutralizes the positive charge of the quaternary nitrogen. In order to prove this assumption experimentally, it was necessary in some way to remove the deactivating effect of the substituted imino group. For this purpose, an electrophyllic group was introduced in conjugation with the second hetero atom. Initially, a nitro group introduced into position 5 (6) was chosen for this purpose.



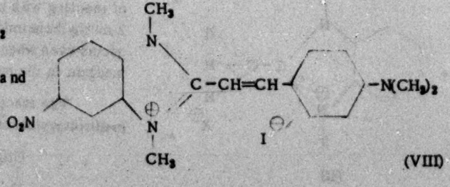
(VI)

The synthesis of this compound (VI) was effected in two stages, 2-Methyl-5(6)-nitrobenzimidazole was obtained by the nitration of 2-methylbenzimidazole, which was then subjected to methylation in a sealed tube with methyl iodide [4]. The 2,3-dimethyl-5(6)-nitrobenzimidazole obtained readily reacted with m-nitro- and p-dimethylaminobenzaldehyde forming the condensation products (VII) and (VIII), the first of which, 3-methyl-2-m-nitrostyryl-5(6)-nitrobenzimidazole methiodide was a yellow, needle-like crystalline substance.



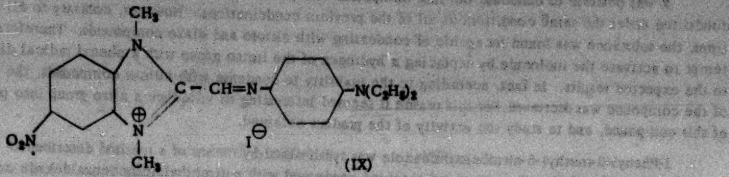
(VII)

and



(VIII)

In addition to the condensation products with aldehydes, the corresponding azomethine (IX) was obtained by the condensation of 2,3-dimethyl-5(6)-nitrobenzimidazole methiodide with p-nitrosodiethylaniline.

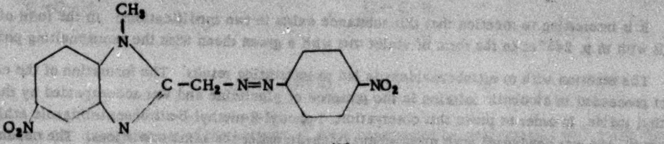


(IX)

This product, which was a dark violet needle like substance with a green sheen, was readily hydrolyzed by the action of dilute acids with the formation of the corresponding aldehyde, which condenses with p-nitrophenylhydrazine to an orange hydrazone. The structure of the hydrazone remains undetermined up to now, since its compoisition according to the results of elementary analysis did not correspond to that calculated theoretically, and in addition, it did not contain iodine

The greatest interest lies in the ability of 2-methyl-5(6)-nitrobenzimidazole methiodide to participate in azo coupling reactions with diazo compounds. The reaction proceeds in aqueous pyridine medium with the elimination of the methyl iodide occurring during the process of formation of the dye, which was indicated by the absence of a halogen in the dye obtained, and which was also confirmed by the determination of the elementary composition of the latter.

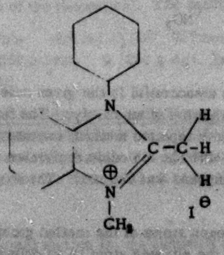
The dye obtained from diazotized p-nitroaniline was a dark violet powder which was difficult to purify. After thorough purification, it can be obtained in the form of a dark green crystalline substance whose structure is expressed by the formula (X).



(X)

Establishing, therefore, the effect of the nitro group, a supplementary activation of the methyl group was attempted by other means. It seemed entirely possible to achieve the same effect by substituting the hydrogen of the imino group by some sort of an electrophyllic group, as for example, a phenyl radical.

The synthesis of 1-phenyl-2-methylbenzimidazole was effected in several steps starting from o-nitrochlorobenzene. The latter was condensed with aniline by means of a method reported in the literature, but containing several changes. The o-nitrodiphenylamine was reduced with sodium sulfite to 2-aminodiphenylamine, from which 1-phenyl-2-methylbenzimidazole [5] was obtained by treatment with acetic anhydride and 4N hydrochloric acid. Two products were obtained upon methylating it: a white crystalline methiodide of 1-phenyl-2-methylbenzimidazole (XI), and the dark brown ones of its periodide (XII).



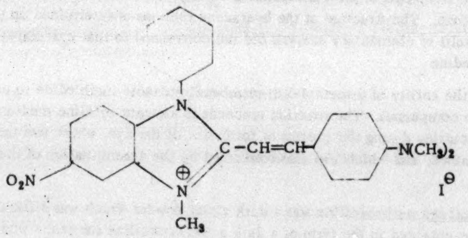
(XI)

$C_{15}H_{15}N_2I \cdot I_2$

(XII)

It was possible to condense the first compound with p-dimethylaminobenzaldehyde. The reaction was conducted under the same conditions as all of the previous condensations. However, contrary to all expectations, the substance was found incapable of condensing with nitroso and diazo compounds. Therefore, the attempt to activate the molecule by replacing a hydrogen of the imino group with a phenyl radical did not lead to the expected results. In fact, according to the inability to condense with nitroso compounds, the activity of the compound was decreased. For this reason it seemed interesting to introduce a nitro group into position 5 of this compound, and to study the activity of the product obtained.

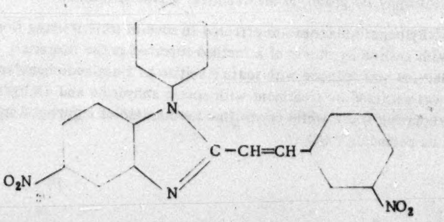
1-Phenyl-2-methyl-5-nitrobenzimidazole was synthesized by means of a method described in the literature [6]. It was found that the compound obtained condensed with p-dimethylaminobenzaldehyde only upon boiling in acetic anhydride; the structure of the condensation product corresponds to formula (XIII).



(XIII)

It is interesting to mention that this substance exists in two modifications: in the form of red-orange crystals with m.p. 245° or in the form of violet ones with a green sheen with the same melting point.

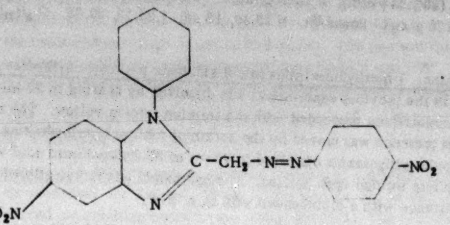
The reaction with m-nitrobenzaldehyde led to interesting results. The formation of the condensation product proceeded in alcoholic solution in the presence of piperidine and was accompanied by the elimination of methyl iodide. In order to prove this observation, 1-phenyl-2-methyl-5-nitrobenzimidazole ethiodide was synthesized, and was condensed with m-nitrobenzaldehyde under the same conditions. The condensation product was found to be identical with that obtained from the methiodide derivative, after thorough purification. The melting point, mixed melting point, as well as the analytical data, were found to be completely identical. Therefore, the structure of this compound may be represented by formula (XIV).



(XIV)

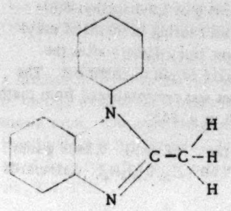
Condensation attempts with nitroso compounds were also unsuccessful in the given case. However, the azo coupling reaction in aqueous pyridine medium led to the formation of an azo dye. The formation of the dye was also accompanied by the loss of methyl iodide. The above reported method was used to prove the structure of the azo dye obtained; i.e., a coupling was effected with the ethiodide derivative. A product, completely identical with the dye obtained from the methiodide compound was obtained. The structure of the dye, therefore, can be represented by the formula (XV).

In addition to the methods for the activation of the hydrogen atoms of the methyl group of 2-methylbenzimidazole reported above and consisting mainly of the conversion of the nitrogen atom to an onium state, it seemed of interest to attempt this activation by introducing electrophyllic groups into the imidazole ring. These groups should

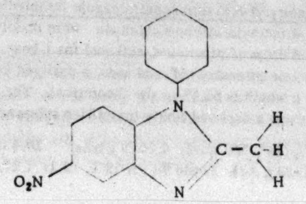


(XV)

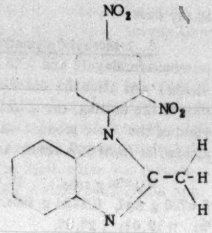
have increased the activity of the methyl group hydrogens by shifting the electrons of the nitrogen atoms toward themselves. The following were chosen as examples: 1-phenyl-2-methylbenzimidazole (XVI), 1-phenyl-2-methyl-5-nitrobenzimidazole (XVII), and 1-(2,4-dinitro)-phenyl-2-methylbenzimidazole (XVIII)*.



(XVI)



(XVII)



(XVIII).

Since there are no data on tests of the activity of these compounds by condensation with aldehydes or nitroso compounds, condensation experiments were conducted with these compounds. The ability to react under mild conditions was of interest as a means of determining the degree of their activity. However, not even one of these compounds was able to react with aldehydes or nitroso compounds in low boiling solvent media. Even the replacement of an imino group hydrogen by such a strong acidifying radical as dinitro phenyl did not lead to a noticeable increase in the activity of the methyl group.

EXPERIMENTAL

1. 3-Methyl-2-m-nitrostyrylbenzimidazole methiodide. A mixture of 2.9 g of 1,2-dimethylbenzimidazole methiodide, 1.5 g of m-nitrobenzaldehyde, 10 ml ethyl alcohol were refluxed for 1 hour. The reaction was catalyzed with 5-10 drops of piperidine which was added before the heating. The starting substances first dissolved, and then as the heating progressed, a yellow condensation product precipitated from the solution. This product was purified by treating it with hot alcohol, and by recrystallization from water. The yield of the product was 1.7 g which is 40% of the theoretical. The product is a pale yellow crystalline substance with m.p. 293°.

0.1101 g. subs. 9.8 ml N_2 (24°, 757 mm). 0.1154 g subs. 10.1 ml N_2 (24°, 757 mm). 0.2490 g subs. 0.1382 g AgI. 0.2252 g subs. 0.1250 g AgI. Found % N 10.2, 10.0; I 30.0, 30.02. $C_{17}H_{16}O_2N_3I$. Calculated %: N 9.97; I 30.16.

2. Azomethine from 1,2-Dimethylbenzimidazole methiodide and p-Nitrosodimethylaniline. The condensation of 1,2-dimethylbenzimidazole methiodide with p-nitrosodimethylaniline was conducted under conditions essentially analogous to the above. The condensation product separated from the solution after cooling in the form of violet crystals with m.p. 270°. It crystallized from methyl or ethyl alcohol.

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* See the experimental section for the synthesis of 1-(2,4-dinitro)-phenyl-2-methylbenzimidazole.

0.1120 g subs.: 13.1 ml N_2 (25°, 754 mm). 0.1092 g subs.: 12.8 ml N_2 (25°, 754 mm). 0.2133 g subs.: 0.1188 g AgI. 0.2120 g subs.: 0.1178 g AgI. Found %: N 13.49, 13.46; I 30.13, 30.05. $C_{18}H_{21}N_4I$. Calculated %: N 13.3; I 30.24.

3. Cleavage of the azomethine: 1-methylbenzimidazole-2-aldehyde p-nitrophenylhydrazone. 0.42 g of the azomethine (substance obtained in the previous experiment) was dissolved by heating in 25 ml of 3% hydrochloric acid. The hydrolysis of the azomethine proceeded with the solution turning yellow. The aldehyde could not be isolated from the solution. Its presence was proved by the action of p-nitrophenylhydrazine. For this purpose the calculated amount of p-nitrophenylhydrazine dissolved in 25 ml of 3% hydrochloric acid was added to the solution. A yellow flocculent precipitate formed upon boiling. The hydrazone was recrystallized from 50% acetic acid; it was a yellow crystalline substance with a bluish sheen with m.p. 270°.

0.1122 g subs.: 15.8 ml N_2 (24°, 764 mm). 0.1236 g subs.: 17.3 ml N_2 (24°, 764 mm). 0.1760 g subs.: 0.0939 g AgI. 0.1538 g subs.: 0.0819 g AgI. Found %: N 16.23, 16.13; I 28.89, 28.8. $C_{16}H_{17}O_2N_5I$. Calculated %: N 15.98; I 28.99.

4. Attempts to couple 1,2-dimethylbenzimidazole methiodide with p-nitrophenyldiazonium. Attempts at azo coupling were made in water, glacial acetic acid, and pyridine. The formation of an azo dye did not occur in any case.

5. 1-Methyl-2-dimethylaminostyryl-5(6)-nitrobenzimidazole methiodide. 1.65 g of 1,2-dimethyl-5(6)-nitrobenzimidazole and 0.75 g of p-dimethylaminobenzaldehyde were dissolved with heating in 20 ml of ethyl alcohol and after the addition of 4-5 drops of piperidine, refluxed for 1 hour. Almost immediately after the start of the boiling, the solution became intensely red, and soon, a dark red precipitate began to come out. The yield of the crude product was 1.25 g which is 55.5% of the theoretical. The product was recrystallized from methyl alcohol or from 80% acetic acid; it was a dark-red, finely crystalline substance with m.p. 248°.

0.1034 g subs.: 10.9 ml N_2 (24°, 762 mm). 0.0979 g subs.: 10.4 ml N_2 (24°, 762 mm). 0.1428 g subs.: 0.0720 g AgI. 0.2424 g subs.: 0.1230 g AgI. Found %: N 12.1, 12.1; I 27.31, 27.59. $C_{19}H_{21}O_2N_4I$. Calculated %: N 12.07; I 27.37.

6. 1-Methyl-2-m-nitrostyryl-5(6)-nitrobenzimidazole methiodide. This compound was obtained by means of an analogous condensation of the methiodide derivative with m-nitrobenzaldehyde. 1.1 g of the condensation product was obtained from 1.65 g of the methiodide, which is 50% of the theoretical. The product was recrystallized from 80% acetic acid. Yellow, fine needles with m.p. 265° were obtained.

0.0898 g subs.: 9.4 ml N_2 (24°, 760 mm). 0.1010 g subs.: 10.6 ml N_2 (24°, 760 mm). 0.1608 g subs.: 0.0814 g AgI. 0.2170 g subs.: 0.1090 g AgI. Found %: N 12.05, 12.1; I 27.36, 27.2. $C_{17}H_{15}O_4N_4I$. Calculated %: N 12.0; I 27.25.

7. Azomethine from 1,2-dimethyl-5(6)-nitrobenzimidazole methiodide and p-nitrosodiethylaniline. The preparation of the azomethine from 1,2-dimethyl-5(6)-nitrobenzimidazole methiodide and p-nitrosodiethylaniline was effected under the same conditions as in the previous condensation. After cooling the solution, 1.1 g of violet crystals separated (from 1.65 g of the starting methiodide). This is a yield of 45% of the theoretical. After recrystallization from ethyl alcohol, the product was obtained in the form of shiny dark green needles with m.p. 202°.

0.1101 g subs.: 13.7 ml N_2 (24°, 764 mm). 0.1012 g subs.: 12.7 ml N_2 (24°, 764 mm). 0.1832 g subs.: 0.0873 g AgI. 0.2010 g subs.: 0.0954 g AgI. Found %: N 14.33, 14.45; I 25.76, 25.66. $C_{19}H_{24}O_2N_5I$. Calculated %: N 14.2; I 25.76.

8. Hydrolysis of the azomethine. Preparation of the hydrazone. 1.1 g of the azomethine obtained in the previous experiment was dissolved with heating in 50 ml of hydrochloric acid. 0.3 g of p-nitrophenylhydrazine dissolved in 3% hydrochloric acid was added to the yellow solution. The mixture was boiled for 15 minutes. An orange flocculent precipitate formed during the boiling. After recrystallization from acetic acid, the product was obtained in the form of fine needles with m.p. 270°, which reversibly change color upon heating. It did not contain iodine.

9. Coupling of 1,2-dimethyl-5(6)-nitrobenzimidazole methiodide with p-nitrophenyldiazonium. 3.3 g of the methiodide derivative was dissolved in 300 ml of water, 40 ml of pyridine was added, and a solution of p-nitrophenyldiazonium, obtained by diazotizing 1.4 g of p-nitroaniline in the usual manner, was added gradually to this solution, cooled to +5°. A dark precipitate formed with the addition of the diazo solution, which was allowed to settle at the end of the reaction. The yield of the crude product was 2.4 g, which is 50% of the theoretical. To purify the product, the impurities were extracted with petroleum ether in a Soxhlet apparatus. The

residue after the extraction was boiled with a small amount of methyl alcohol for a final removal of the impurities which were more soluble in the alcohol than the dye. The product was converted into a crystalline state during this processing, while the color changed from violet to dark green. The dye was then dissolved in pyridine, filtered, and precipitated with water. The melting point of the pure product was 266°. The dye was readily soluble in pyridine and dioxane with an intense violet color. It was partially soluble in alcohol and acetone with a dark red color.

0.1126 g subs.: 24.5 ml N_2 (24°, 754 mm). 0.1048 g subs.: 22.9 ml N_2 (24°, 754 mm). Found %: N 24.8, 24.91. $C_{15}H_{12}O_4N_6$. Calculated %: N 24.71.

10. Preparation of o-Nitrophenylene diamine. 31.5 g of o-nitrochlorobenzene was refluxed with 40 g of aniline, using an air condenser for 3 hours. The reaction product was poured into water, acidified with hydrochloric acid, and the unreacted o-nitrochlorobenzene was steam distilled. The reaction product separated from the remaining mixture after cooling in the form of a black precipitate from which o-nitrodiphenylamine was removed by extraction with petroleum ether in a Soxhlet apparatus. Pure o-nitrodiphenylamine precipitated from the petroleum ether upon cooling in the form of orange crystals with m.p. 75°.

11. Phenyl-o-phenylenediamine (o-Aminodiphenylamine). A mixture of 5 g of o-nitrodiphenylamine and 20 g of sodium sulfite in 50 ml of ethyl alcohol was refluxed for 1.5-2 hours with efficient stirring. The mixture was then diluted with water, acidified with hydrochloric acid, and boiled to precipitate the sulfur. After filtration of the sulfur, o-aminiodiphenylamine was precipitated with ammonia. It melted at 79-80° after recrystallization from a mixture of alcohol and water.

12. 1-Phenyl-2-methylbenzimidazole methiodide. 1-Phenyl-2-methylbenzimidazole, obtained by means of a method reported in the literature [7], was heated with an equimolecular amount of methyl iodide in the presence of methyl alcohol for 4 hours in a sealed tube at 140°. The contents of the tube crystallized in the form of a light brown mass. The reaction product was treated with warm methyl alcohol in order to separate 1-phenyl-2-methylbenzimidazole methiodide. The insoluble part was a brown crystalline periodide. The methiodide was precipitated from the alcoholic solution with ether. It was obtained in the form of white, needle-like crystals with m.p. ite, 217-218°.

0.1200 g subs.: 8.7 ml N_2 (24°, 752 mm). 0.1775 g subs.: 12.6 ml N_2 (24°, 752 mm). 0.1470 g subs.: 0.0982 g AgI. 0.1880 g subs.: 0.1258 g AgI. Found %: N 8.24, 8.07; I 36.33, 36.19. $C_{15}H_{15}N_2I$. Calculated %: N 8.00; I 36.28.

13. 1-Phenyl-2-p-dimethylaminostyrylbenzimidazole methiodide. 1.75 g of 1-phenyl-2-methylbenzimidazole methiodide and 0.75 g of p-dimethylaminobenzaldehyde were boiled with several drops of piperidine in ethyl aclohol solution for 1 hour. The solution gradually became intense red After cooling and dilution with water, the impure reaction product had the form of an oily mass. After treatment with benzene, the product solidified in the form of a red powder which was obtained in the form of bright red needle-like crystals with m.p. 179-180° after recrystallization from water. The yield of the product was 1.5 g after treatment with benzene, which is 62.2% of the theoretical.

0.1182 g subs.: 9.1 ml N_2 (24°, 762 mm). 0.1074 g subs.: 8.3 ml N_2 (24°, 762 mm). 0.2355 g subs.: 0.1150 g AgI. 0.2014 g subs.: 0.0980 g AgI. Found %: N 8.85, 8.9; I 26.4, 26.32. $C_{24}H_{24}N_3I$. Calculated %: N 8.7; I 26.4.

14. Attempts to Condense 1-Phenyl-2-methylbenzimidazole methiodide with p-Nitrosodimethylaniline. An attempt to condense the starting products in alcoholic solution in the presence of piperidine was unsuccessful. Upon diluting the solution with ether, the starting imidazole was recovered.

15. Attempted Azo Coupling of 1-Phenyl-2-methylbenzimidazole methiodide. Attempts were made to azo couple with p-nitrophenyldiazonium in alcohol, glacial acetic acid, and pyridine. However, these attempts did not lead to positive results.

16. 1-Phenyl-2-p-dimethylaminostyryl-5-nitrobenzimidazole methiodide. 2 g of 1-phenyl-2-methyl-5-nitrobenzimidazole methiodide, synthesized according to a literature method [6], and 0.75 g of p-dimethylaminobenzaldehyde was boiled for 1 hour with 10 ml of acetic anhydride. The solution acquired a claret color with the boiling. After cooling, violet needles with a green sheen separated from the solution. The yield of the product was 1.5 g which is 56.4% of the theoretical. Upon recrystallization from acetic anhydride, orange-red crystals with m.p. 245°, or violet needles with a green sheen with the same melting point were obtained. The same result was obtained upon recrystallization from alcohol. It must, however, be mentioned that the violet crystals are easily obtained from alcohol, and the orange-red from acetic anhydride.

Analysis of the red product:

0.1104 g subs.: 10.5 ml N_2 (24°, 752 mm). 0.1088 g subs.: 10.3 ml N_2 (24°, 752 mm). 0.1478 g subs.: 0.0667 g AgI. 0.2110 g subs.: 0.0940 g AgI. Found %: N 10.81, 10.76; I 24.41, 24.09. $C_{24}H_{23}O_2N_4I$. Calculated %: N 10.66; I 24.14.

17. Condensation with m-Nitrobenzaldehyde. The condensation of 2 g of 1-phenyl-2-methyl-5-nitrobenzimidazole methiodide with an equimolecular amount of m-nitrobenzaldehyde was effected in alcohol in the presence of piperidine. A yellow precipitate formed upon boiling, whose yield was 1.2 g which is 61.5% of the theoretical. For purification, the product was treated with hot alcohol and benzene, then dissolved in pyridine, and precipitated with water. The purified product melted at 220° (with decomposition).

0.1120 g subs.: 0.2122 g CO_2; 0.0370 g H_2O. 0.0991 g subs.: 12.5 ml N_2 (23°, 769 mm). 0.1010 g subs.: 12.8 ml N_2 (25°, 770 mm). Found %: C 65.1; H 3.7; N 14.7, 14.63. $C_{21}H_{14}O_4N_4$. Calculated %: C 65.28; H 3.62; N 14.5.

18. 1-Phenyl-2-methyl-5-nitrobenzimidazole ethiodide. 5 g of 1-phenyl-2-methyl-5-nitrobenzimidazole was heated with 2 ml of ethyl iodide and 5 ml of ethyl alcohol for 4 hours at 140° in a sealed tube. The reaction product, a brown crystalline mass, was treated with methyl alcohol; the ethiodide separated from the solution upon the addition of ether in the form of yellow crystals with m.p. 266°.

0.2032 g subs.: 18.3 ml N_2 (23°, 760 mm). 0.1864 g subs.: 17 ml N_2 (23°, 760 mm). 0.2127 g subs.: 0.1220 g AgI. 0.3039 g subs.: 0.1736 g AgI. Found %: N 31.03, 30.89; I 10.39, 10.52. $C_{16}H_{16}O_2N_3I$. Calculated %: N 31.06; I 10.27.

19. Condensation of the Ethiodide with m-Nitrobenzaldehyde. 1.6 g of 1-phenyl-2-methyl-5-nitrobenzimidazole ethiodide was condensed with 0.6 g of m-nitrobenzaldehyde, keeping the conditions of the condensation of the methiodide with m-nitrobenzaladehyde. The purified condensation product had the same melting point (220°). A mixed sample of both products melted at 220°.

0.1214 g subs.: 0.2900 g CO_2; 0.0412 g H_2O. 0.1100 g subs.: 13.8 ml N_2 (24°, 768 mm). Found %: C 65.2; H 3.79; N 14.6. $C_{21}H_{14}O_4N_4$. Calculated %: C 65.28; H 3.62; N 14.5.

20. Attempts to Condense 1-Phenyl-2-methyl-5-nitrobenzimidazole methiodide with p-Nitrosodimethylaniline. An attempt was made to condense the above products in alcohol with the addition of piperidine or sodium carbonate. Neither in the first or the second case was the expected product obtained. The starting imidazole was recovered from the solution by means of ether.

21. Coupling of 1-Phenyl-2-methyl-5-nitrobenzimidazole methiodide with p-Nitrophenyldiazonium. 4 g of the methiodide was dissolved in 500 ml of water and 40 ml of pyridine. A diazo solution prepared from 1.4 g of p-nitroaniline and neutralized with sodium acetate, was added dropwise to this solution at 0°. A violet color appeared, and the formation of a dark precipitate occurred. The precipitate was allowed to settle and was filtered. To remove the impurities from the dye, it was extracted with petroleum ether, and then boiled with ethyl alcohol. A partial solution of the dye occurred, but the main part of the dye remained undissolved and was converted to the crystalline state, as a result of which it changed from violet to dark green. After such treatment, the dye was dissolved in pyridine, and then precipitated from the solution with water. The pure product melted at 292°.

0.1012 g subs.: 0.2225 g CO_2; 0.0320 g H_2O. 0.0676 g subs.: 12.3 ml N_2 (23°, 762 mm). 0.0824 g subs.: 15.1 ml N_2 (23°, 762 mm). Found %: C 60.0; H 3.53; N 21.04, 21.18. $C_{20}H_{14}O_4N_6$. Calculated %: C 60.12; H 3.5; N 20.82.

22. Coupling of 1-Phenyl-2-methyl-5-nitrobenzimidazole ethiodide with p-Nitrophenyldiazonium. The coupling of the ethiodide was conducted under the same conditions as that of the methiodide. The product obtained melted at 292° after thorough purification.

0.1104 g subs.: 0.2428 g CO_2; 0.0355 g H_2O. 0.0987 g subs.: 18 ml N_2 (23°, 762 mm). Found %: C 60.02; H 3.59; N 21.09. $C_{20}H_{14}O_4N_6$. Calculated %: C 60.12; H 3.5; N 20.89.

23. 2-Amino-2,4-dinitrodiphenylamine. 20.2 g of dinitrochlorobenzene was mixed with 10.8 g of o-phenylene diamine. 8.2 g of sodium acetate and 50 ml of ethyl alcohol were added to the mixture which was then boiled on the water bath for 1 hour. A crystalline precipitate formed upon boiling which consisted of a mixture of red rhombic and yellow needle-like crystals. After cooling, the precipitate was filtered and washed with hot water to remove the sodium chloride formed. The yield of the condensation product was 22 g which is 80.5% of the theoretical. The product was recrystallized from alcohol and glacial acetic acid. Yellow needles formed upon rapid cooling in the first, and in the second case a mixture of yellow and red crystals upon slow cooling. The yellow,

as well as the red product melted at 151°. The yellow substance reddened when close to the melting point.

Analysis of the red product:

0.1156 g subs.: 0.2220 g CO_2; 0.0391 g H_2O. 0.1248 g subs.: 0.2395 g CO_2; 0.0435 g H_2O. 0.1181 g subs.: 10.9 ml N_2 (24°, 764 mm). 0.1205 g subs.: 21.4 ml N_2 (24°, 764 mm). Found %: C 52.4, 52.37; H 3.78, 3.81; N 20.52, 20.6. $C_{12}H_{10}O_4N_4$. Calculated %: C 52.55; H 3.65; N 20.43.

24. 2-Acetylamino-2,4-dinitrodiphenylamine. 2.75 g of 2-amino-2,4-dinitrodiphenylamine was boiled for a short time with 2 ml of acetic anhydride and 10-15 ml of acetic acid. The substance went into solution upon boiling, from which bright yellow, scaly crystals separated after cooling. The yield of the product was 2.9 g which is 92% of the theoretical; m.p. 235°.

It was hydrolyzed upon prolonged boiling with 4N hydrochloric acid with the formation of the hydrochloride and, of the starting 2-amino-2,4-dinitrodiphenylamine. The latter was a yellow crystalline substance with m.p. 147°. It was recrystallized from dilute hydrochloric acid; even boiling with water converted it into the starting 2-amino-2,4-dinitrodiphenylamine.

Analysis of the acetyl derivative:

0.1218 g subs.: 0.2294 g CO_2; 0.0403 g H_2O. 0.1065 g subs.: 0.2031 g CO_2; 0.0357 g H_2O. 0.1182 g subs.: 18.2 ml N_2 (25°, 762 mm). 0.1202 g subs.: 18.6 ml N_2 (25°, 762 mm). Found %: C 51.4, 51.32; H 3.7, 3.75; N 17.78, 17.9. $C_{14}H_{12}O_5N_4$. Calculated %: C 51.53; H 3.58; N 17.7.

25. 2-Diacetylamino-2,4-dinitrodiphenylamine. 5.5 g of 2-amino-2,4-dinitrodiphenylamine was heated with 20 ml of acetic anhydride for 2 hours at 180° in a sealed tube. The contents of the tube were a yellow crystalline substance after cooling. The yield of the product was 6.1 g which is 85.2% of the theoretical. After recrystallization from alcohol, the product was obtained in the form of light yellow, shiny platelets with m.p. 189° (with decomposition). Even upon short boiling in alcoholic solution in the presence of several drops of piperidine, the product eliminated one acetyl group, and was transformed into the monoacetyl derivative.

0.1156 g subs.: 0.2265 g CO_2; 0.0423 g H_2O. 0.1311 g subs.: 0.2569 g CO_2; 0.0447 g H_2O. 0.1212 g subs.: 16.8 ml N_2 (25°, 756 mm). 0.1014 g subs.: 13.8 ml N_2 (24°, 756 mm). Found %: C 53.46, 53.47; H 4.09, 3.82; N 15.85, 15.55. $C_{16}H_{14}O_6N_4$. Calculated %: C 53.63; H 3.91; N 15.6.

26. 1-(2,4-Dinitro)-phenyl-2-methylbenzimidazole. 3 g of the diacetyl derivative was heated with 20 ml of 4N hydrochloric acid for 2 hours at 170° in a sealed tube. After opening the tube, the transparent solution was poured into a beaker, diluted with 50 ml of water, and the reaction product precipitated with ammonia. The yellow precipitate was filtered, dried, and recrystallized from benzene. The yield of the crude product was 2.35 g, which is 94% of the theoretical. After recrystallization, the product was obtained in the form of yellow shiny platelets with m.p. 179°. The product was also recrystallized from dilute alcohol.

0.1244 g subs.: 0.2562 g CO_2; 0.0389 g H_2O. 0.1155 g subs.: 0.2377 g CO_2; 0.0372 g H_2O. 0.1048 g subs.: 17.2 ml N_2 (23°, 762 mm). 0.1136 g subs.: 18.7 ml N_2 (23°, 762 mm). Found %: C 56.2, 56.1; H 3.5, 3.6; N 18.90, 19.03. $C_{14}H_{10}O_4N_4$. Calculated %: C 56.39; H 3.36; N 18.79.

As stated above, 1-(2,4-dinitro)-phenyl-2-methylbenzimidazole, in spite of the presence of a strong electrophillic residue (dinitrophenyl) in the molecule, was found to be incapable of participating in condensations with aldehydes and nitroso compounds under various conditions.

SUMMARY

1. The main factor in the increase of the activity of a methyl group is the positive charge on the nitrogen atom in conjugation with this group. This charge directly strengthens the polarization of the carbon hydrogen bond in the methyl group.

2. The effect of nitro, phenyl, and dinitrophenyl groups conjugated with the imino group of the imidazole ring can only be considered indirect, and results from the blocking of the unshared pair of electrons of the second nitrogen atom, and in the same way as in the case of the presence of an onium nitrogen, to remove the possibility of decreasing the positive charge of the nitrogen atom. The strongest supplementary activating group in this case is the nitro in position 5 of the benzimidazole ring.

3. The above groups do not have any noticeable effect on the methyl group when introduced into an imidazole ring which lacks an onium nitrogen.

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* See Consultants Bureau Translation, page 1721.

CLEAVAGE OF LIGNIN WITH METALLIC SODIUM IN LIQUID AMMONIA

VI. ACTION OF METALLIC SODIUM IN LIQUID AMMONIA ON FIR WOOD

A. F. Semechkina and N. N. Shorygina

Several years ago, the authors found that lignin isolated from fir wood was cleaved by the action of metallic sodium in liquid ammonia at −33° into low molecular substances among which a considerable part were phenolic derivatives of phenylpropane. It was also shown that natural lignin not isolated from the wood was also cleaved by analogous treatment under the same conditions with the formation of phenolic substances soluble in ether [1-6].

Freudenberg and co-workers [6] treated fir wood flour with metallic potassium in liquid ammonia solution at 20°. The wood was cleaved into the following components: cellulose with a yield of 46-48% of the weight of the wood used, which contained nono-cellulose impurities; lignin with a yield of 26-28% of which a part (16-18%) of the weight of the wood, was soluble in methanol, part (3%) was soluble in 1% acetic acid, and part (7-8%) was insoluble in these solvents, but was soluble in dilute alkalies, and 3-pentosans with a yield of 5% of the weight of the wood. According to Freudenberg, the main part of the pentosans was destroyed by metallic sodium in ammonia. Freudenberg isolated no individual lower molecular compounds.

It seemed important to determine whether or not phenols which were isolated from copper ammonium fir lignin, are obtained by the cleavage of natural lignin (unisolated from the wood fibers). An affirmative answer would show the close resemblance between the structures of natural and isolated lignin.

In contrast to Freudenberg, who worked with small amounts of wood (5 g of fir flour), the authors treated 30-50 g of fine fir shavings with metallic sodium solution in one experiment. The reaction was conducted at a temperature below the boiling point of ammonia. As a result, the wood was cleaved into the following components: cellulose with a yield of 34.4%, hemicelluloses, with a yield of 8.3%, and lignin with a yield of 9.2%. In addition, lower molecular products soluble in ether were obtained with a yield of 7.5%, and products of the destruction of carbohydrates and lignin soluble in water, with a yield of 12.3%. 28% of the weight of the wood could not be accounted for. The cellulose was a light, almost white, fibrous material, with the following composition: (in %): C 44.0, H 6.38, OCH_3 0.99. The hemicelluloses (substances soluble in alkali and insoluble in alcohol), which were a powder-like product, had the composition (in %): C 44.76, H 6.45, OCH_3 2.03.

The presence of methoxyl groups in the cellulose, as well as in the hemicelluloses, even with a somewhat lower carbon content, is of great interest. It indicates that the presence of methoxyl groups is not caused by impurities of the lignin hydrocarbons, which are completely separated under the reaction conditions used, but are the result of the presence of these groups in the carbohydrates themselves.

An analogous conclusion was made by Freudenberg for beech wood carbohydrates. He obtained substances of carbohydrate character containing a considerable amount of methoxyl groups by the treatment of beech wood with metallic potassium in liquid ammonia. Freudenberg did not mention anything on the formation of methylated carbohydrates from fir wood on treating it with potassium in liquid ammonia.

Dihydroeugenol was isolated from the ether-soluble lower molecular products of the decomposition of the wood, and was identified in the form of the benzoate. Characteristically, a considerably higher amount of lower molecular phenolic substances, based on the amount of lignin in the wood (24.75% of the weight of the lignin determined in the wood by means of the sulfuric acid method) was obtained from the fir wood by a single treatment with metallic sodium in liquid ammonia, than from the isolated lignin (about 8%). The lower molecular substances were obtained with a total yield 28% only after many treatments of the copper ammonium fir lignin with a solution of sodium in liquid ammonia [1].

The yield of the lignin obtained from the fir wood upon treatment with metallic sodium in liquid ammonia was found to be very small, and was only 9.2% of the weight of the wood (30.33% of the amount of lignin determined in the wood by the sulfuric acid method). The lignin had the form of a yellowish powder, the following composition (in%): C 60.55, H 6.58, OCH_3 9.45. The methoxyl groups content in the lignin must be explained by the fact that part of them contained in the lignin were cleaved under the conditions of the reaction. If the amount of lower molecular acidic products, which were soluble in ether formed during the cleavage with metallic sodium, and which were, evidently, obtained from the lignin, was added to the amount of lignin isolated from the reaction mixture, then the total yield of the lignin would be 9.2 + 7.5 = 16.7%.

Part of the products of the destruction of the lignin can be found in the water soluble decomposition products, since these products are always formed to an extent of about 20% of the isolated lignin during the treatment with a solution of sodium in liquid ammonia. If these results are conditionally applied for natural lignin, too, then the amount of lignin, together with its destruction products, is again increased by 6.06% (20% of 30.3%), and is, therefore, 16.7 + 6.06 = 22.76% of the weight of the wood. The yield, based on the "sulfuric acid lignin" contained in the wood, is equal to 75.1%.

It is interesting that Freudenberg and co-workers separated almost all of the lignin contained in the wood by treating wood flour with a solution of metallic potassium in liquid ammonia at 20°. A considerable amount (16 - 18% of the weight of the wood) contained 15.36% of methoxyl groups, i.e., it was only slightly changed lignin (it was soluble in CH_3OH).

An intense decomposition of part of the lignin to lower molecular substances occurred in the author's experiments.

The fact of the easy separation of the lignin from the carbohydrates leads to the suggestion that it is bound with the carbohydrate components in the walls of the vegetable skeleton by chemical bonds which are readily cleaved by metallic sodium.

It is known that simple ether bonds are cleaved by metallic sodium under these conditions with a varying degree of facility, which depends on their nature. Aromatic ethers are cleaved very easily, aralkyl less readily, and the aliphatic, not at all [7, 8]. The presence of aromatic ether bonds in the lignin carbohydrate complex is impossible. Aliphatic ether bonds are excluded on the basis of experimental results. Therefore, only the aralkyl ether bond remains. However, on the basis of the known facts, it is difficult to imagine how aralkyl ether bonds could be cleaved quantitatively under the conditions of the experiment.

It is known that glucosides with aliphatic aglucones are not cleaved by sodium, but glucosides with aromatic aglucones are in certain cases. Thus, phenylglucoside was cleaved by metallic potassium in liquid ammonia [6]. Coniferin is partially cleaved by a solution of metallic sodium in liquid ammonia; arbutin, however, is not cleaved at all [8].

It is possible that the carbohydrates are combined with lignin in the vegetable fibers by means of ketal or poly-ketal bonds resulting from the keto groups in the lignin and the hydroxyl groups in the carbohydrates. It is regrettable that up to now there are no data on the stability of ketals from the lignin type keto groups and the hydroxyl groups of carbohydrates to the action of sodium in liquid ammonia. We know, however, that benzophenone dimethyl ketal is almost completely cleaved by a solution of sodium in liquid ammonia at −33° [8].

EXPERIMENTAL

A piece of the trunk of a freshly-cut 25-year old fir, cut 1 m from the root and 2 m in length, was cleaned from cork and was converted into thin shavings. An average sample of the shavings was dried in a desiccator over phosphoric anhydride, and analyzed.

Composition of the wood: cellulose, by the chloroform method, 53.4%, pentosans (according to Tollins), 11.2% lignin by the F. P. Komarov modification of the sulfuric acid method, 28.4%.

30 g of the shavings was extracted twice by an alcohol-benzene mixture (1 : 1) and treated 2 times at room temperature with a 5% solution of sodium hydroxide with shaking in order to remove the hemicellulose part. The shavings were washed with water, 2% acetic acid solution, and again with water, and dried first in the air, and then over phosphorus pentoxide The yield of the purified shavings was 91.4% of the starting ones. The amount of lignin in the shavings treated in this manner was 30.3% (according to F. P. Komarov's method).

The absolutely dry shavings were poured into a reaction vessel, placed in a large Dewar vessel, and covered with 1000 ml of liquid ammonia; 100% of the weight of the wood of metallic sodium was added to it in several portions. The reaction mass was stirred daily. The reaction was completed in 7 days (decolorization of the ammonia solution). Moist ether was added to the residue after the removal of the ammonia, and the reaction mixture was left to stand overnight; the ether was then poured off, and water was added to the residue. A considerable amount of the reaction mass dissolved.

Isolation of cellulose. The entire mass was extracted with ether, the water-insoluble residue was filtered from the alkaline solution, washed with dilute alkali solution, then with water, and dried, first in the air, and then over P_2O_5. 10.32 g cellulose was obtained in the form of an almost white fibrous material. It had the following elementary composition:

4.261, 4.308 mg substance: 6.870, 6.845 mg CO_2; 2.430, 2.440 mg H_2O. Found %: C 44.00, 43.99; H 6.38, 6.37. $C_6H_{10}O_5$. Calculated %: C 44.44; H 6.15. 16.56, 15.67 mg substance: 1.6, 1.49 ml 0.02 N $Na_2S_2O_3$. Found %: OCH_3 1.0, 0.98.

Isolation of the lower molecular phenolic substances. The aqueous alkali solution remaining after the removal of the cellulose, was extracted with ether. The ether extracts were dried, and the ether was removed. The residue, 0.37 g (1.23% of the weight of the wood), was a transparent, oil-like, light yellow liquid. It was vacuum distilled at 0.1 mm. 0.2 g of an almost colorless oil-like liquid was obtained.

0.2 g of the substance, 1.2 g of benzoyl chloride, and 10 g of a 15% sodium hyroxide solution were shaken, whereby a crystalline mass formed rapidly. The crystals melted at 74° after recrystallization from alcohol. A mixed melting point with dihydroeugenol benzoate gave no depression.

The aqueous alkali solution after extraction with ether, was acidified to Congo with 10% sulfuric acid. A voluminous precipitate of lignin and hemicelluloses formed. The mixture (acidic solution and precipitate) was extracted many times with ether. The ether extracts were dried, and the ether was removed.

1.88 g of a thick dark liquid (6.27% of the starting wood) was obtained. The liquid was distilled at 0.1 mm. Two fractions were obtained, and a considerable amount of the substance tarred.

Fraction 1 boiled below 100° at 0.1 mm and was a clear mobile oil; 0.45g.

3.360 mg substance: 8.825 mg CO_2; 2.634 mg H_2O. Found %: C 71.66; H 8.77. $C_{10}H_{14}O_2$ · (dihydroeugenol). Calculated %: C 72.28; H 8.43.

The substance formed a crystalline benzoate melting at 68-71° upon shaking with benzoyl chloride and alkali.

5.130 mg substance: 14.284 mg CO_2; 2.559 mg H_2O. Found %: C 75.67; H 6.44. $C_{17}H_{18}O_3$. Calculated %: C 75.53; H 6.71.

The benzoate obtained melted at 68-71° when mixed with dihydroeugenol benzoate. A mixed sample with eugenol benzoate (m.p. 68-70°) gave a depression and melted at 57-60°. Therefore fraction 1 obtained by the distillation of the ether extracts of the acidified reaction mixture was also dihydroeugenol.

Fraction 2, a thick, syrupy liquid boiled above 100° at 0.1 mm; it was not identified.

Isolation of lignin. The precipitate which formed on the acidification of the alkaline solution with 10% sulfuric acid, was filtered, after the extraction of the entire mass with ether, on a glass filter, and then treated many times with hot alcohol. The combined alcoholic extracts were dried with anhydrous sodium sulfate, and the alcohol was distilled in vacuum to a small volume. The liquid was poured into a small dish and left in a vacuum desiccator over sulfuric acid. Several days later, the dry residue was transferred into a desiccator containing phosphorus pentoxide

The yellowish powdered dry lignin weighed 2.76 g (9.2% of the weight of the wood taken).

4.027, 4.405 mg substance: 8.931, 9.780 mg CO_2; 2.378, 2.630 mg H_2O. 19.04 mg substance: 17.36 ml 0.02 N $Na_2S_2O_3$. Found %: C 60.52, 60.58; H 6.66, 6.51; OCH_3 9.43.

2 g of the lignin obtained was covered with 100 ml of liquid ammonia; part of the lignin dissolved, the other part became plastic and was converted into a soft state. 2 g of metallic sodium was added to the mixture, and the reaction and the processing were conducted in the usual manner. The low molecular products were not investigated because there was very little of them, and the undecomposed lignin was analyzed.

3.538, mg substance: 8.395 mg CO_2; 2.070 mg H_2O; 4.94 ml 0.02 N $Na_2S_2O_3$. Found %: C 64.75; H 6.55; OCH_3 9.08.

Isolation of the hemicelluloses. After the removal of the lignin, the alcohol-insoluble residue was dried, first in the air, and then over P_2O_5. The hemicelluloses obtained were in the form of a grayish powder.

7.070, 6.915 mg substance: 11.545, 11.370 mg CO_2; 4.065, 4.006 mg H_2O. 4.84 mg substance: 0.93 ml 0.2 N $Na_2S_2O_3$. Found %: C 44.56, 44.87; H 6.43, 6.47; OCH_3 1.97. $C_6H_{10}O_5$. Calculated %: C 44.44; H 6.15. $C_5H_8O_4$. Calculated %: C 45.46; H 7.04.

SUMMARY

1. Fir wood was readily cleaved into its components by treatment with a solution of metallic sodium liquid ammonia at −33°.

2. The isolated polysaccharides, cellulose and hemicelluloses contained a small amount of methoxyl groups which indicated that not all of the methoxyl groups in the fir wood were contained in the lignin; part of them belonged to the carbohydrate.

3. The lignin was decomposed to a great extent by the action of metallic sodium in liquid ammonia on the wood. 7.5% of the weight of the wood or 24.6% of the lignin, determined by the sulfuric acid method, was converted into lower molecular substances soluble in ether, and partly vacuum distillable.

4. Dihydroeugenol, previously obtained from isolated lignin by treating it with metallic sodium in liquid ammonia, was isolated from the destruction products of the lignin. This indicated the close relationship between isolated and natural lignin.

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* See Consultants Bureau English translation, page 1569.

** See Consultants Bureau English translation, page 1243.

*** See Consultants Bureau English translation, page 1095.

INVESTIGATION OF THE ALKALOIDS OF SENECIO SPECIES

IX. STRUCTURE OF THE ALKALOIDS OF THE SPIRAL RAGWORT (SENECIO SARRACENIUS)

A. Danilova and A. Kuzovkov

The alkaloid sarracine $C_{18}H_{27}O_5N$, which is the ester of platinecine, and its N-oxide, were isolated by the authors from the spiral ragwort as reported in communication VIII [1].

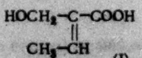
The present investigation is concerned with the structure of the acids which esterify platinecine. An acid with m.p. 43-44° was formed by the hydrolysis of sarracine with 10% hydrochloric acid, which was identified as cis α,β-dimethylacrylic (angelic)-acid [2]. In addition to angelic acid, a second acid, named sarracinic acid by the authors, was also isolated.

Sarracinic acid has the composition corresponding to the formula $C_5H_8O_3$, is readily soluble in water and in alcohol, contains one hydroxyl group, forms a zinc and a silver salt, does not have a sharp melting point, and is very difficult to purify [3, 4]. Sarracinic acid is unsaturated in character and decolorizes potassium permanganate in sulfuric acid solution. Acetaldehyde and formaldehyde, identified as the dimedon compounds, were obtained by the oxidation of sarracinic acid with lead peroxide in 5% phosphoric acid. Sarracinic acid does not form a lactone upon heating with 10% sulfuric acid, which indicates that the hydroxyl group is in the α- or β-position to the carboxyl.

1,5 moles of hydrogen is absorbed by the catalytic reduction of sarracinic acid with a platinum catalyst, and a mixture of two acids is formed, which can be separated by their different volatility with steam. Methylethylacetic acid (A) was obtained from the steam distillable part, which was identified by means of the preparation of its amide and by direct comparison with the synthetic methylethylacetamide. The isolation of methylethylacetic acid completely determined the carbon skeleton structure of sarracinic acid. Acid (B) nonvolatile with steam, was a non-crystalline thick substance readily soluble in water and in alcohol, which did not decolorize a sulfuric acid solution of permanganate. It, judging by its composition, is dihydrosarracinic acid.

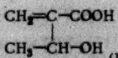
The procedure of the catalytic reduction in two directions with the formation of an acid minus a hydroxyl group, in addition to the normal reduction product, indicated the presence of the allylic grouping $-CH{=}CH-\underset{\displaystyle OH}{\underset{|}{CH}}-$ [5].

All of the experimental data obtained agreed satisfactorily with three possible formulas for the structure of sarracinic acid:



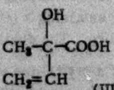
$$HOCH_2-\underset{\displaystyle CH_3-CH}{\underset{\|}{C}}-COOH$$

(I)



$$CH_2{=}\underset{\displaystyle CH_3-CH-OH}{\underset{|}{C}}-COOH$$

(II)



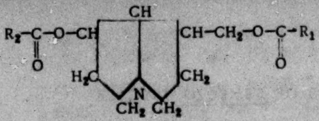
$$CH_3-\overset{\displaystyle OH}{\overset{|}{\underset{\displaystyle CH_2{=}CH}{\underset{|}{C}}}}-COOH$$

(III)

However, there is still insufficient data to choose one of the three possible formulas.

By comparing the structure of sarracine with that of platinecine, angelic, and sarracinic acid, it is easily apparent that the molecule of the alkaloid is formed from these three parts by the esterification of the two hydroxyl groups of the three possible for the compositions of platinecine and sarracinic acid, by the acids.

In order to determine whether one or both of the hydroxyl groups of platinecine were esterified in the formation of sarracine, it was reacted with thionyl chloride under conditions which assured the substitution of all of the possible free hydroxyl groups of platinecine by a halogen [6], the chloro derivative was reduced catalytically with a platinum catalyst, and the reaction product was saponified. As a result of all of these transformations, platinecine was isolated, which meant that both of the hydroxyl groups were esterified in the formation of sarracine. If a free OH group had been present in the aminoalcohol, then isoretronecanol or retronecanol would have been obtained. Therefore, two structural formulas can be proposed for sarracine:



I. R_1COOH = sarracinic acid
R_2COOH = angelic acid

II. R_1COOH = angelic acid
R_2COOH = sarracinic acid

The second alkaloid which is sarracine N-oxide, has a corresponding structure.

EXPERIMENTAL

1. Hydrolysis of Sarracine with 10% Hydrochloric Acid

50 ml of 10% HCl was added to 10 g of sarracine, and the mixture was refluxed on the screen for 4 hours. During the saponification, one of the acids formed was distilled and was deposited in the balls of the condenser. At the end of the hydrolysis, the distilled acid was dissolved in ether. After the removal of the ether, 1.3 g of a crystalline acid with m.p. 43-44.5° was obtained, which did not give a melting point depression with synthetic angelic acid.

The acidic aqueous solution was steam distilled until the absence of an acidic reaction in the distillate. The distillate was extracted with ether, and 1.2 g of angelic acid was obtained after the removal of the ether. The acidic aqueous solution was concentrated on the water bath to a volume of 10 ml and extracted with ether. After the removal of the ether, 2 g of a non-crystalline acid of thick consistency was obtained. which was called sarracinic acid by the authors.

The sarracinic acid was subjected to elementary analysis to constant weight. but no consistant results were obtained The following results were obtained by a determination of the hydroxyl groups by Tserevitinov's method: OH 30.76, 26.86. $C_5H_8O_3$. Calculated %: OH 29.31.

Zinc salt of sarracinic acid. 1 g of sarracinic acid was dissolved in 5 ml of water. Crystalline zinc carbonate was added to the solution until the evolution of carbon dioxide stopped. The excess zinc carbonate was filtered and washed with 2 ml of water. The filtrate was evaporated to dryness. The zinc salt was a thick glass-like mass which was converted into a powder by rubbing with ether. The salt was readily soluble in water and alcohol. It was precipitated as a colorless residue from an alcoholic solution with ether. The weight of the salt obtained was 0.45 g. The zinc salt could not be recrystallized and did not have a sharp melting point.

Silver salt. 0.5 g of sarracinic acid was neutralized with 5% aqueous ammonia solution, and an 0.1 N solution of silver nitrate was added to the neutralized solution until the formation of a precipitate stopped. The precipitated salt was filtered, washed with water, and dried in a vacuum desiccator until constant weight. The silver salt did not have a sharp melting point.

3.207 mg substance: 3.119 mg CO_2; 0.880 mg H_2O. 3.28 mg substance: 3.213 mg CO_2; 0.930 mg H_2O. Found %: C 26.54, 26.72; H 3.07, 3.17. $C_5H_7O_3Ag$. Calculated %: C 26.29; H 3.14.

2. Oxidation of Sarracinic Acid with Lead Peroxide

1.7 g of sarracinic acid, 3.5 g of lead peroxide, and 14 ml of 5% phosphoric acid were placed into a round-bottomed flask containing a reflux condenser. The mixture was heated for 3 hours on the boiling water bath, and then steam distilled. The distillate was collected in a receiver cooled with ice.

0.27 g of a crystalline substance with m.p. 135-138° was obtained from the first 200 ml fraction of the distillate with a 1% aqueous solution of dimedone. The melting point was 139-140° after recrystallization from petroleum ether. No depression was found in a mixed melting point of the compound obtained and synthetic dimedone acetaldehyde.

0.2 g of a crystalline substance with m.p. 180-182° was obtained from the second and third fractions with an aqueous solution of dimedon. The melting point of the substance was 186-187° after recrystallization from petroleum ether. No depression was found in a mixed melting point of the compound obtained and synthetic dimedone formaldehyde.

3. Catalytic Reduction of Sarracinic Acid

1.56 g of sarracinic acid was dissolved in 50 ml of alcohol, 0.2 g of platinum catalyst was added, and it was reduced by shaking with hydrogen. 450 ml of hydrogen was absorbed in 1 hour.

The catalyst was filtered, the alcohol removed through dephlegmator by heating on the water bath. The reduced acid was steam-distilled until the absence of an acidic reaction in the distillate. The distillate was extracted with ether, the ether solution was dried over Na_2SO_4. After the removal of the ether, 0.8 g of a liquid acid which was steam-volatile (A) was obtained.

The aqueous solution from which the steam-volatile acid was distilled, was concentrated by heating on the water bath to a volume of 5 ml and extracted with ether.

After the removal of the ether, 0.52 g of a non-crystalline acid which did not decolorize a sulfuric acid solution of potassium permanganate, (B) was obtained.

Preparation of acid (A) amide. 0.5 g of acid (A) was placed into a flask connected to a reflux condenser; 5 g of PCl_5 was added, and the mixture was heated for 15 minutes on the water bath. The solution obtained was poured from the yellow precipitate which formed, and cooled in an ice bath. 10 ml of 28% aqueous ammonia solution was added dropwise to the cooled solution. The mixture obtained was extracted with ether in a separatory funnel. The ether solution was dried over Na_2SO_4. After the removal of the ether, 0.12 g of a crystalline substance with m.p. 109-111° was obtained; it did not give a depression in a mixed melting point with synthetic methylethylacetamide.

4. Action of Thionyl Chloride on Sarracine, Reduction of the Product Obtained, and Hydrolysis

2 g of sarracine, dried to constant weight, was placed into a round-bottomed flask containing a reflux condenser and a dropping funnel. 10 g of freshly distilled thionyl chloride was added dropwise while it was cooled externally with an ice and salt bath. After the addition of the thionyl chloride, the mixture was heated for 30 minutes to 70°, cooled, and poured on ice. The aqueous solution was made alkaline with 10% ammonia and extracted with ether. The ether was dried over Na_2SO_4, filtered, and distilled. The weight of the substance obtained was 1.78 g. Without purification, the substance was dissolved in 20 ml of alcohol, 0.2 g of platinum catalyst was added, and it was reduced by shaking with hydrogen. The reduction stopped after 65 ml of hydrogen was absorbed.

The catalyst was filtered and washed with alcohol. 25 ml of 0.5 N alcoholic alkali was added to the alcoholic solution, and it was boiled by heating on the water bath for 3 hours. The alcoholic solution was filtered, and the alcohol removed. The residue was extracted many times with chloroform. After removal of the chloroform, 0.9 g of a crystalline substance with m.p. 140-142° was obtained. The m.p. was 147-149° after recrystallization from acetone. No depression in mixed melting point of the substance obtained and platinecine was found.

The analyses were performed by the co-workers of the microanalytical laboratory of the All-Union Chemico-Pharmaceutical Scientific Research Institute under the direction of V. V. Kolpakova.

SUMMARY

1. It was shown that the new alkaloids sarracine and sarracine N-oxide, isolated from the spiral ragwort, were diesters of the amino alcohol platinecine and cis-α,β-dimethylacrylic acid (angelic acid), and an unsaturated acid of the composition, $C_5H_8O_3$, called sarracinic acid by the authors.

2. It was shown that sarracinic acid has the carbon skeleton of methylethylacetic acid and differs from it by the presence of a hydroxyl group and a double bond.

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* See Consultants Bureau English translation, page 1485.

A. M. BUTLEROV

(1828—1886)

THE 125TH ANNIVERSARY OF THE BIRTH OF THE FOUNDER OF THE THEORY OF CHEMICAL STRUCTURE AND OF THE SYSTEMATIC SYNTHESIS OF ORGANIC COMPOUNDS

S. N. Danilov

The scientific acitivity of Aleksandr Mikhailovich Butlerov covering the period between the fifties and the eighties of the last century, was already highly acclaimed by his leading contemporaries. The further we move from the years of his activity the clearer it becomes that his scientific studies directed organic chemistry to new routes of multistage synthesis, to the investigation of isomeric, tautomeric and polymeric transformations, to the establishment of the chemical structure of complex compounds, and to the clarification of the mechanism of chemical reactions.

The theoretical and experimental investigations of A. M. Butlerov are characterized by innovations and great penetration. They astonish us by the wealth of their scientific insight, originality and experimental accuracy, by their most valuable discoveries and undertakings. The most important experimental results of his researches were directed toward the founding and development of the theory of chemical structure which for upward of 90 years has had a profound and progressive influence upon the development of organic chemistry and the whole of chemical science. The theory of chemical structure, whose author was A. M. Butlerov, must be regarded as one of the greatest generalizations of science.

In the past the great services of A. M. Butlerov in the theoretical field have sometimes been underrated and even forgotten. Even today the same lack of appreciation of his work may be noticed. It must therefore be emphasized that Butlerov is indeed the founder, the architect of a theory of chemical structure differing fundamentally and in principle from the previous theoretical concepts [1].

Science is indebted to him for the logical application of the principles of materialistic philosophy to the study of the structure and properties of molecules.

Characteristic of Butlerov is the materialistic and even dialectical solution of the fundamental problems of organic chemistry in contrast to the unrealistic eclectic and idealistic approaches of Gerrard, Kekulé, Kolbe, Berthelot and other great chemists of the mid-nineteenth century to the fundamental chemical problems.

The 125th anniversary of the birth of Butlerov fell on September 6, 1953 (he was born on August 15, 1828 in the town of Chistopol, Kazan province): it is memorable not only because of the work of the great scientist but also because the intervening 125 years have been a notable historical period in the development of organic chemistry. This is true in particular of the last 90 years, after Butlerov's theory of chemical structure had been confirmed by him in collaboration with his students in the sixties.

The growth of industry and the development of capitalism (also in Russia) from the second quarter of the nineteenth century led to more and more new problems in the chemistry of organic compounds. A very active study of natural organic compounds commenced and there was rapid development of the branches of industry involving the chemical processing of natural products such as bituminous coal (illuminating gas), petroleum, starch (K. S. Kirchoff, 1806-1815) and others. But after Butlerov's theory of chemical structure had become generally accepted as a basic principle of organic chemistry, the vast material of that science was brought into a harmonious system and the systematic laboratory and industrial synthesis of organic compounds was developed.

Toward the end of the twenties of the nineteenth century, when Butlerov was born, organic chemistry had already collected not a few valuable observations and discoveries; the composition and properties of important natural compounds such as fats were being industriously studied.

The first three decades of the past century and the subsequent years up to the start of the sixties constituted a preparatory period in the development of the theoretical ideas of organic chemistry which rounded off the Butlerov theory of chemical structure.

The forties to the sixties was a period in which interest was shown not only in the systematics and classification of the very many organic compounds that were already known, but also in the problems of linking and arrangement of atoms in the molecules of organic substances. Between the sixties and the death of Butlerov (1886) organic chemistry was enriched by notable theoretical and experimental researches of Butlerov himself and his pupils. Even during his lifetime the enormous significance of the theory of chemical structure had become manifest and the discoveries which had been made by Butlerov himself in the experimental field were beginning to be widely disseminated.

Butlerov's theory of chemical structure was further developed in the field of stereochemistry by the investigations of Louis Pasteur, Van't Hoff and Le Bel, Wislicenus and others, while Butlerov himself made a valuable contribution to the concepts of the spatial distribution of atoms in molecules.

Taking into consideration the great revolution in chemistry and the vast perspectives revealed to synthetic organic chemistry through Butlerov's theory of chemical structure, we can distinguish the following fundamental stages in the history of organic chemistry:

1) The pre-Butlerov period (before the start of the sixties of last century) — a period of accumulation of the most important experimental facts and of the creation of a classification of organic compounds (homologous series, etc.); in this period various conflicting ideas were reconciled by several fundamental concepts of chemistry and some basic ideas were developed for the future theory of organic chemistry.

2) The Butlerov period — the period of creation and introduction into science of the theory of chemical structure and the development of stereochemistry on its basis.

3) The post-Butlerov period, marked by the extensive development of the organic synthesis of new compounds and of the important substances of the vegetable and animal kingdoms, as well as by the strengthening of the theory of chemical structure with special reference to the reciprocal effects of atomics and groups of atoms in molecules.

A. M. Butlerov began his work as an experimental and theoretical organic chemist in the fifties, in a period of sharp controversy in scientific chemical ideas, and he fertilized the researches of his contemporaries by indicating new vistas and the great potentialities of chemical development.

As a scientist, Butlerov grew up at Kazan University [2] as a student of eminent chemists: K. K. Klaus, discoverer of the element ruthenium, and N. N. Zinin, famed for the reduction of nitrobenzene to aniline and other reactions.

Starting to deliver lectures at Kazan University at the age of 21-22, Butlerov at once distinguished himself as a talented and versatile lecturer. At the early age of 26 he was chosen as professor at Kazan University where he worked from 1850 to 1869. In 1869, when we was called to Petersburg University as professor, began the not less glorious Petersburg period of his activity as a scientist and teacher. In Petersburg, just as in Kazan, Butlerov directed research in the laboratory and was always surrounded by numerous students. In 1871 he became a member of the Russian Academy of Sciences, and in 1874 he was elected academician extraordinary.

With his penetrating philosophical intellect and great mastery of experimental chemistry, Butlerov founded the renowned Butlerov school of science whose representatives were found first in Kazan and later in Petersburg University and the Academy of Sciences.

The members of the Butlerov school were the pride of our science.

Brilliant lecturer, talented teacher and inspired scientist, he rendered great service to the teaching and development of organic chemistry in Russia.

A. M. Butlerov combined scientific work with serious social activity, thus following the custom of the progressive Russian Intelligentsia — "six decades" in the national interest.

He undertook much public work as professor and rector of Kazan University, as professor at Petersburg University and as Academician (in the latter capacity as active member), and as President between 1879 and 1882 of the Russian Physicochemical Society, as Chairman of the Free Economic Society and propagandist of efficient bee-keeping, as a great worker for the education of women, and so on.

Aleksandr Mikhailovich Butlerov — scientist-patriot, scientist-citizen — fought both in the university and in the Academy for the interests of Russian science with great rectitude and passion.

A. M. Butlerov died suddenly at the age of 58 on August 17 (Old Style August 5), 1886 in the village of Butlerovko in the Spassky district of Kazan province where he was also buried.

Chemists of the Soviet Union are assiduously engaged in the development of the theory of chemical structure, working fruitfully in the field of organic synthesis for the solution of the most important theoretical and practical problems.

In connection with the 125th anniversary of the birth of our great compatriot, A. M. Butlerov, Soviet chemists with great gratitude again take note of the most important of his scientific researches from which stem the great achievements of organic chemistry in the USSR.

1. The Molecular-Atomic Constitution of Substances and the Atomic Weights of the Elements According to Butlerov's Ideas

In his scientific work Butlerov was a materialist who regarded a compound as being in movement and in growth. In his researches it is not difficult to see the logical application of atomic-molecular concepts. Only with firm belief in the reality of molecules and atoms was it possible for Butlerov to expound the concept of the strictly determined chemical structure of chemical compounds and of the representation of the composition and structure of a molecule by a unique chemical formula.

In his communication of 1885 [3] we find the following opinions: "The atom is just as real an entity as the molecule" and "in our opinion we must speak of atoms as if they were real objects".

Being convinced that the chemical elements are formed from simpler component particles, Butlerov arrived at the conclusion that certain variations in the atomic weights of elements were possible, as also (in consequence) deviations of the composition of chemical compounds from the law of constant proportions. In the laboratory Butlerov (1882) carried out experiments aiming at clarification of this — for his day — complex problem; these were broken off by his unexpected death.

Butlerov thus made a new approach to the problem of the concept of the chemical element. This fundamental concept had undergone profound changes [5] in the course of centuries; it acquired new features with the discovery of radioactivity and the detection of isotopic phenomena which had been so astonishingly predicted by Butlerov.

Very effective tools for the establishment of differences in the mass of atoms were the physical methods of investigation developed in recent times and stemming directly from the Crookes tube which A. M. was the first to demonstrate in Russia in 1880 at a conference of the physics division of the Russian Physico-Chemical Society. In his ideas on isotopy Butlerov was 30 years in advance of the science of his day.

2. Chemism is Movement

The works of Butlerov ("Introduction to the complete study of organic chemistry" [6], etc.) contain his views on chemical affinity and the units of valences of the elements. These are interesting as a reflection of the ideas of this time on these important questions, which even today have not been conclusively solved. Very important, however, is his general dictum in regard to chemical phenomena: "Chemism is movement".

According to Butlerov, therefore, chemical phenomena are a special form of motion which may be manifested in thermal, optical and electrical phenomena. He draws attention to the "importance of the relation between the chemical action of electricity and the concept of atomicity which plays such an important part in chemical theory" and to the equivalence between electricity, heat, chemism and visible mechanical work. In opposition to Berzelius he did not consider it possible to equate chemical phenomena with electrical phenomena but held the opinion that chemism is a more general and complex form of motion. It must be remembered that, according to Butlerov, the atoms entering into the composition of molecules are in continuous movement [7]. "We look upon a chemical compound not as on a dead and motionless thing; we assume, on the contrary, that it is endowed with constant movement; this is true also of its minutest particles whose reciprocal relative continuous movements are resolved into a certain constant average result." However, as long as a given substance exists, this movement of the atoms is executed with maintenance of the previous "order of the chemical bond between the atoms in the molecule, and this constitutes the chemical structure of the substance".

"We provisionally say" —we read in another of his communications (1885) [3]—"that atoms are combined or joined with one another, but we definitely do not thereby imply that the atoms actually grip one another or that they are relatively immobilized."

In his communication (in Speyer in 1861) [8] on the theory of chemical structure, Butlerov reasoned about the linkage strain in polyatomic molecules on the assumption that it may change "according to the nature of the actual substances and according to the conditions in which the action takes effect." Consequently, a difference in the units of affinity of carbon could be assumed. At first, as long as it was not known that ethyl hydride and dimethyl were both ethane (this was established in 1864 following the work of Schorlemmer), and as long as other cases of suggested isomerism had not been clarified, Butlerov suggested the hypothesis of different units of affinity in polyvalent elements. But after starting a more detailed study of the isomerism of hydrocarbons, he arrived at the conclusion that the isomeric parafinic hydrocarbons can only differ in the structure of the hydrocarbon sketeton. In the paper on "the affinity of polyatomic partners" [9] we see the transition from his concept of the difference in units of affinity to the idea of the mutual influence of atoms constituting a molecule: "Here and now, when speaking of the difference in units of affinity, it is impossible not to point to the influence which is exreted on the properties of one set of units of affinity by the nature of the partners linking the other units, and it is even necessary to add that the difference is perhaps governed by this influence."

Butlerov afterwards expressed himself several times in opposition to the hypothesis of difference of units of affinity when deriving possible structural isomers; thus he criticized the application of this hypothesis by Kekulè who had erroneously written of the existence of three propyl alcohols (1865-1866). This hypothesis was for a long time adhered to by Erlenmeyer who was a follower of Butlerov in questions of the theory of chemical structure. On the same basis Kolbe erroneously reported the existence of two methylpropyl ketones. When triphenylmethyl, tribiphenylmethyl, etc., became known, their existence was ascribed to the phenyl and (in particular) the biphenyl radicals attracting more affinity to themselves than usual from the carbon atom of methane. Reference began to be made to the differing affinity capacity (capacité affinitaire) of radicals, i.e., the differing consumption of the affinity of the carbon atom by different radicals (A. Werner) [10].

In his last communication to the Academy of Sciences (1943) A. E. Favorsky [12] returned to the hypothesis of the different quotas of affinity disbursed by the carbon atom in binding different substituents, but he modified the hypothesis by introducing the concept of a supplementary affinity of the carbon atom.

Much attention was given in the twenties and thirties of the present century to the question of the affinity capacity of different radicals.

Many authors have arranged radicals in order of affinity capacity on the basis of many reactions and not infrequently with conflicting results. Thus in the dehydration of glycols and the isomerization of aldehydes to ketones we obtain contradictory series in respect of migration ability and affinity capacity [11].

The concept of the affinity capacity of atoms and radicals, as formulated by A. Werner, as well as the idea of the changing "strain" of chemical bonds or the difference in relative magnitude of the consumed affinity about which both Butlerov and Erlenmeyer speculated (to some extent also Kolbe—in respect of carbonic acid) may be expediently considered in the light of the electronic hypothesis of the variation in the density of the electron cloud which varies for different atoms, i.e., the so-called electron density.

Butlerov established [13] that, contrary to Erlenmeyer's view, isomerism in the light of the theory of chemical structure is not the result of a hypothetical difference in the units of affinity attached to polygenic atoms.

Butlerov's idea of the mobility of atoms in a molecule ("dynamics, not statics") was clearly expressed in his theories of isomeric and tautomeric phenomena which A. E. Favorsky later described in the concept of equilibrium isomerism [14] and illustrated by his own experiments (transformations of mono- and dibromohydrins of alcohols, reversible isomerization of mono- and disubstituted acetylenes and allenes). He showed that isomeric transformations also acquire an equilibrium character in certain conditions, as is typical of tautomeric phenomena.

Butlerov persistently directed attention to the importance of applying dynamic ideas to chemical phenomena. Butlerov gave the following definition of a chemical compound [7]: "A chemical compound constitutes a specific relation between the movements of the atoms in a molecule."

The actual existence of the very same number of isomers for a given structure as is predicted by the theory of chemical structure is a most vivid confirmation of the theory of chemical structure.

Butlerov and his pupils started a close study of the isomeric transformations accompanied by rearrangement of atoms in a molecule. The first (and clear) example of intramolecular rearrangement of a carbon skeleton (1874) was the pinacolin rearrangement [15]. Even earlier (1868) Butlerov had noted the formation of a secondary alcohol instead of a tertiary one, in the organozinc synthesis [16]. The study of isomeric transformations was very extensively developed by A. E. Favorsky and his school.

Discussing the formulas [17] of cyanic acid and urea, Butlerov in 1862 arrived at the conclusion that for cyanic acid we may picture "the still existent but transient phase of its structure which may exist, for example, during conversion of cyanic acid into carbon dioxide and ammonia".

In studies [18] on "isodibutylene" (diisobutene) interesting conclusions were reached in connection with the problem of the addition of water to olefinic hydrocarbons and the reverse process which is accompanied by isomerization: "We think that even in the absence of a catalyst (which may be sulfuric acid in this example) the molecules of some substances, due to the constant breadkown and re-formation of products in a fresh order, are constantly isomerizing, changing from one modification into another — and conversely." Butlerov's great scientific perspicacity suggested to him the possibility of an equilibrium shift in a specific direction, a process found to be characteristic of the equilibrium mixture of tautomeric substances: "The mass of a compound contains particles with different structures (say two) and when these molecules are susceptible to rearrangement the whole of this mass will naturally undergo reactions characteristic of one of the structures or reactions characteristic of the second structure, depending upon the nature of the reagents employed, i.e., depending upon the direction of the effect of this reaction."

In 1885 Laar [19] proposed the term "tautomerism" for the phenomena discovered by Butlerov, but Laar idealistically misinterpreted them by attributing an oscillating character to the transformations and a multiple molecular structure to the molecules of one and the same substance, instead of speaking about an equilibrium mixture of tautomeric compounds.

3. The Chemical Structure of Molecules and Its Representation by Chemical Formulas

A fundamental law of chemistry was formulated in Butlerov's theory of chemical structure: Inherent in each chemical compound is a strictly defined order of the reciprocal chemical linking of the atoms constituting its molecule, all the properties of a compound being governed by its chemical structure, while the chemical properties of the atoms and groups of atoms in the molecule — linked to one another or not directly linked — depend on their reciprocal effects and the external conditions.

Chemical structure is established unambiguously by chemical (synthetic and analytical) and physical methods. A chemical formula — one unique for each chemical compound — must reflect "the mode of the mutual chemical bonding of the elementary components (atoms) in the molecule". Butlerov also wrote [6]: "It would be correct, in the present state of knowledge, to apply the term 'rational formulas' only to formulas which reflect the chemical structure of molecules."

The problem of the arrangement of atoms in a molecule, already posed in a general form by M. V. Lomonosov, began to receive ever increasing attention after the development of methods of quantitative analysis of organic compounds and the introduction of chemical formulas for the elementary composition with representation of each chemical element and its relative amount by the first letters of the Latin name (Berzelius, 1813).

On the basis of the old radical theory, which merged with the electrochemical hypothesis of Berzelius, chemical formulas indicated two simple or more complex portions which, so to speak, "preexist" in the molecule in question. Thus, the formula of saltpeter would indicate that potassium nitrate consists of anhydrous nitric acid and potassium oxide, while the formulas of organic compounds are represented by "preexistent" radicals for which an independent existence was originally postulated.

In our own time the application of the idea of "preexistence" of one complex body in another can be seen in the usual formulas of molecular compounds. Characteristic of typical complex compounds are more complex relations between the components of the molecule, but also in these formulas a sort of "preexistence" is attributed to simpler molecules in the compounds (in ammines, hydrates, etc.).

The problem of molecular compounds has been adequately clarified by A. Werner's theory with reference to typical complex compounds.

Concerning compounds for which it is difficult to decide "whether we are dealing with chemical molecules or aggregates of molecules which adjoin one another", Butlerov [7] spoke as follows (1879) about molecular compounds: "We have no criteria as yet for strict demarcation of a chemical molecule from an aggregate of molecules, while the transition of the latter into solutions, etc., is quite gradual and imperceptible."

We know that physicochemical analysis in the hands of D. I. Mendeleev, N. S. Kurnakov and their pupils made a valuable contribution to our understanding of solutions, melts, and molecular compounds.

According to Gerrard's unitary theory, in harmony with Liebig's theory of polybasic acids, the suggestion was made of the "preexistence" in sulfuric acid of sulfur trioxide and water, while salts were regarded as constituted by metallic oxide and acid; the molecule was thus regarded as a unit. The unitarists had a different conception of organic compounds. "Radicals (wrote Butlerov apropos of the unitary theory) are those groups which are encountered in the composition of different complex substances; they have the ability to be transferred by certain reagents from one substance to another and may thus be regarded as replacing certain elementary particles" [6].

The formulas consequently indicated that in a typical substance (hydrogen, water, hydrogen chloride, ammonia) the hydrogen atoms are replaced by organic radicals. However, the concept of types, according to Butlerov, "does not represent an inherent, material subscription to the unitary theory but a close merging with the latter" [6].

The principle of substitution found wide application in organic and inorganic chemistry, especially with the introduction into science of the doctrine of atomicity of elements (Frankland, 1852; Odling, 1854, etc.). In particular, the quadrivalence of carbon was established by Kekulé and Kolbe. Dumas equated the substitution principle with Mitscherlich's doctrine of isomorphism, but the similarity is remote.

Kolbe, who for a long time remained an adherent of the theory of radicals and an opponent of the theory of chemical structure, combined the former with the ideas [7] of substitution which he used extensively and in some cases with successful results. He pointed to the possibility of existence of secondary and tertiary alcohols (1859), and effected substitution of the hydrogens in a radical of a simpler alcohol by other radicals. But by utilizing arbitrary methods in applying the substitution principle, he frequently fell into error, as for instance in assuming the existence of two methylpropyl ketones.

In Butlerov's paper (1864) [20] "on the systematic application of the principle of atomicity" to the prediction of isomerism and metamerism, we find the following passage: "How faulty become derivations when substitution is brought into the foreground and the theory of chemical structure (constitution or points of application of affinity) is put on one side."

N. A. Menshutkin [21] for a long time expressed himself (1878, 1885) against the theory of chemical structure and attempted to show that the isomerism of hydrocarbons can be quite satisfactorily explained by the substitution theory without reference to the theory of structure.

The French chemist Berthelot, who had acquired a great reputation in the first half of the 19th century by his successful syntheses of simple organic compounds, adhered in the sixties to the eighties [3] to the same theory of substitution in a slightly modified form (known as the theory of generators); according to his theory, the constitution of a compound is represented by the equation of its formation from a selected generator. Berthelot explained the different properties of isomers by differences in generators (starting substances) and not by different chemical structures.

Berthelot's criticism of the theory of chemical structure was described by Butlerov (in his 1879 paper) as "not chemical realism"; his evaluation of Berthelot's views was summed up in the phrase "chemical nihilism".

The principle of substitution is fundamentally correct, and in the case of simpler compounds, it provides graphic examples for teachers, as is evident for instance from D. I. Mendeleev's utilization of the principle of substitution in "Principles of Chemistry" in the derivation of nitrogen derivatives. However, the principle of substitution-as Butlerov correctly pointed out, is a narrower concept, of secondary importance in comparison with the theory of chemical structure.

In recent years Yu. A. Zhdanov [22] and others have drawn attention to the previously ignored materialistic-dialectical aspect of the theory of chemical structure and to Butlerov's concept of the chemical formula as the reflection of the actual order of the chemical linking of atoms in a molecule. Apart from the immediate pupils [23] of Butlerov such as V. V. Markovnikov, many authors [24] have paid high tribute to the tremendous achievement of Butlerov in firmly introducing into science the theory of chemical structure, but they have not properly demarcated the theory of chemical structure from the doctrine of the valence of elements, from the ideas of the linking of atoms in the molecule, from the principle of substitution and from other inferences from previous theoretical views (homologous series, the concept of radicals) utilized by Butlerov in his theory of chemical structure.

A. M. Butlerov enunciated original ideas on the following aspects:

1) The specific order of chemical bonding of atoms in a molecule.

2) Methods of establishing chemical structure by synthetic, analytical and physical methods.

3) Strict demarcation of the problem of chemical structure in the sense of the order of chemical bonding of atoms from the problem of the spatial arrangement of atoms (constitutional concept of Laurent). Butlerov proposed the tetrahedral model of the carbon atom before Van't Hoff and Le Bel. Butlerov thereby clearly expressed the necessity of explanation of the existence of "physical isomers" (optically active and other isomers) from the standpoint of the spatial arrangement of atoms in the molecule; this must be regarded as a development of the theory of chemical structure.

4) Isomerism as an inevitable consequence of the definite chemical structure of compounds of saturated and unsaturated types with a clear formulation of the concepts of double and triple bonds.

5) Tautomeric, isomeric and polymeric transformations (associated with states of equilibrium) as a consequence of the dynamism of atoms in the molecule which leads to the compounds which are most stable under the given conditions.

6) The doctrine of the chemical formula as the representation of the actual order of the chemical bonding of atoms in the molecule.

It is true that the theory of substitution and the theory of types, and indeed the unitary system and the old theory of radicals and substitution (Kolbe), in no way conflicted with the principle that each chemical compound must be characterized by a single formula. Nevertheless, Gerrard, Kekule and the other "typists" made an unrealistic and generally idealistic approach to this problem. Gerrard stated that we only know the past and future molecules resulting from chemical reactions and not the present molecules. Gerrard and later Kekule (after 1861) considered that as many formulas may be attributed to a chemical compound as there are methods for its preparation. In his 1861 report [8], however, Butlerov wrote: "If we now attempt to specify the chemical structure of substances and if we succeed in expressing it by our formulas, then these formulas will be (not completely but to a certain degree) real and rational formulas. In this sense only one rational formula will be possible for each compound."

In the pages of our chemical [25] and general-philosophical journals, as well as in many symposia [26] it was shown that the polystructurality of the resonance and mesomeric formulas, like the "resonance" of Wheland and the "mesomerism" of Ingold, are completely fallacious and idealistic concepts devoid of any basis in quantum chemistry and radically in conflict with Butlerov's theory of chemical structure.

The representation of the structure of any chemical compound by two formulas between which, as it were, the true structure lies is entirely pointless because each compound is different from any other and the formula expresses the chemical structure. Consequently, the conclusion (in the sense of V. A. Izmailsky's mesomerism) that the structure of a given substance lies between two certain structures, i.e., between two formulas, is meaningless [26]. As long as a chemical structure is not fully proved, we may propose hypothetically one or several formulas.

Chemical structural formulas express the order of the chemical linking of atoms on the basis of a study of the chemical and physical properties of compounds, and therein resides their value for chemistry. There is no doubt also that spatial formulas in organic chemistry and in the chemistry of complexes adequately represent the true geometrical relations of the atoms in molecules.

For the representation of the chemical structure of experimentally prepared molecules, Butlerov made use of the valence concept (Odling, Frankland), of the principles of substitution and of the concept of linking of atoms formulated in the papers of Kekule (1858), Couper (1858) and Loschmidt (1861). Only Couper (before 1861), however, and not Kekule applied the theory of linked atoms to the representation of formulas, and even these formulas bore a formal and abritrary character. Butlerov gave proved chemical formulas for a series of compounds and — on the basis of this materialistic theory of chemical structure —he demonstrated the predictive value of the formulas of the theory of chemical structure in regard to isomers as early as 1863. Finally, the derivation of chemical formulas is founded on the doctrine of the atomic-molecular constitution of substances, of atomic weights and of valence. Butlerov said in his communication of 1885: "What would be the significance, we may ask, of any one of our formulas with its atomic symbols if the concept of the atom did not represent some specific reality for us?"

While representing the order of the chemical bond of atoms, the usual structural formulas do not picture those reciprocal effects of atoms and atomic groupings which are dependent on the chemical structure and the nature of the atoms and which are characteristic of molecules in given conditions. Since the time of Butlerov and Markovnikov, whose work led to the adoption in organic chemistry of the doctrine of the reciprocal influence of atoms, very many diverse rules have accumulated in regard to the mutual influence of atoms, reactive groups and radicals. In this connection Butlerov said: "When general laws become known for the dependence of the chemical properties of substances on their chemical structure, then such formulas (i.e., real rational formulas in Butlerov's sense) will be the expression of all these properties".

In connection with electronic concepts in organic chemistry the problem arises of the clarification and representation by electronic formulas of the mutual effects of atoms in molecules (electronic effects). Unfortunately, it has not so far been possible to arrive at any conclusive results in this connection. The treatment, on the basis of electronic theories, of the vast amount of experimental material on the mutual influences of atoms and atomic groupings with reference to the role of the reactant and the external conditions, represents an important task of organic chemistry, and constitutes a further broadening of Butlerov's theory of chemical structure.

The existing symbolism, i.e., the method of representation on paper of the order of chemical linking or the recording of the formula of a molecule in a plane or in space is a matter of convention.

There also is a need to work out a more expressive symbolism for the representation of the mutual influences of atoms as a first stage in the development of the electronic theory on the basis of the change in density of the electron cloud. The study of the physical characteristics as a supplement to that of the chemical characteristics would also throw light on this aspect of molecular characteristics.

4. The Value of Butlerov's Experimental Investigations

Butlerov was responsible for a great number of notable experimental studies [27] which have long been finding extensive application in science and technology and have been followed up in various directions by chemists in other countries. These investigations are so well known that it is unnecessary to detail them. We may single out for special mention his investigations on the synthesis of isomers of saturated and olefinic hydrocarbons and of monohydric alcohols (especially trimethylcarbinol and other tertiary alcohols). Well-known are his studies on isomeric transformations (the pinacolin rearrangement, etc.).

The synthesis, worked out in detail, of tertiary alcohols by the organozinc method was the start of the fruitful organozinc syntheses of saturated alcohols (A. M. Zaitsev, E. E. Vagner, V. E. Tishchenko and others) and of unsaturated alcohols (Zaitsev alcohols), of hydroxy acids (the Reformatsky synthesis) and of other classes of organic compounds. We know that these organozinc syntheses form the basis of the well-known organomagnesium synthesis which has superseded the organozinc synthesis. In these, just as in other investigations, Butlerov thoroughly investigated the mechanism of the reactions.

His investigations on olefinic hydrocarbons are of considerable importance in science and industry. Previously, little known, Butlerov's work led to this group of compounds finding extensive application. Butlerov developed many addition reactions of olefinic hydrocarbons. He conclusively established the structure of ethylene: in this research he was greatly aided by his synthesis of ethylene when attempting to prepare a free radical (methylene) from methylene iodide.

These studies were linked with his greatest discoveries which related to the synthesis of polymeric formaldehyde and the synthesis therefrom of monoses by the action of lime water. To Butlerov actually belongs the credit of the first synthesis of sugars. This research served for clarification of the structural formula of monoses. Of special significance is the fact that on the basis of this sugar synthesis it was possible to account for the assimilation of carbon dioxide and water in the green parts of plants with formation of starch. Many very important substances, first prepared by Butlerov, are now manufactured in our factories and throughout the world in quantities of many thousands of tons and are valuable products both in themselves and as starting materials for many chemical derivatives (formaldehyde, urotropine, isobutene, diisobutene, etc.). Butlerov reactions form the basis of industrial organic syntheses.

Butlerov's studies on the synthesis of polymeric formaldehyde, the importance of the Butlerov synthesis of monoses for the understanding of the formation of starch in nature, his notable investigations of stepwise polymerization of isobutene, which was the precursor of modern syntheses of polyvinyl compounds and of numerous synthetic rubbers (but no longer by a stepwise mechanism but by chain, radical and ionic mechanisms) —all this justifies us in considering Butlerov to be the founder of the science of high-molecular compounds.

The chemistry of high-molecular compounds, developed on the basis of Butlerov's theory of chemical structure, is also much indebted to Butlerov's other investigations, which gave great impetus to the brilliant development of organic synthesis.

The Butlerov school of chemical science, which includes the names of many famous Russian chemists, has left a permanent mark on the development of chemistry in our land.

Chemists of the USSR, the scientific progeny of Butlerov, true followers of Butlerov, surrounded by the all-embracing solicitude of the Communist Party and the Soviet Government, tirelessly work for the glory of the peoples of the USSR by increasing the scientific wealth created by Butlerov and his pupils.

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THE INTERACTION OF NITRATES AND NITRITES OF METALS OF THE FIRST AND SECOND GROUPS OF THE PERIODIC SYSTEM IN MELTS

VIII. INVESTIGATION OF THE TERNARY SYSTEM OF NITRATES OF SILVER, POTASSIUM AND CADMIUM

P. I. Protsenko

Earlier investigations [1, 2, 3] had shown that nitrates of metals of the first group of Mendeleev's periodic system do not behave identically when reacted with nitrates of cadmium in melts. Thus, the nitrates of lithium and sodium do not enter into chemical reaction with cadmium nitrates but form eutectic mixtures with them. On the other hand, the nitrates of potassium and rubidium manifest a marked tendency to form complexes with cadmium nitrate and form the chemical compounds: $Cd(NO_3)_2 \cdot 2KNO_3$ and $Cd(NO_3)_2 \cdot 2RbNO_3$.

The formation of the above complexes is readily explained on the basis of ionic polarizability. The coefficients of polarizability of cations of lithium and sodium are relatively small (0.029 for the first and 0.187 for the second), whereas those of cations of potassium and rubidium are many times larger (0.888 and 1.49 respectively [4]).

The dipoles formed under the action of their own electromagnetic fields in the molecules of potassium and rubidium nitrates on the one hand and in the cadmium nitrate molecule on the other hand, bring about an orientation corresponding to their poles, in consequence of which the above-mentioned chemical compounds are formed.

On reacting cadmium nitrate with silver nitrate we can expect, in view of the polarizability of the silver ion associated with its position in the periodic system, that chemical reaction would also take place between the components.

In this paper we present experimental material which confirms that the interaction of silver nitrate with cadmium nitrate in melts containing various concentrations of components does actually lead to a chemical compound $Cd(NO_3)_2 \cdot 2AgNO_3$, analogous in composition to the compounds of potassium and rubidium nitrates with cadmium nitrate; the new compound is found to be stable (as will be shown below) even in presence of other components.

EXPERIMENTAL

Binary Systems We have already described [3] the component side of the triangle of the system potassium nitrate – cadmium nitrate. The binary system potassium nitrate – silver nitrate has been investigated by Palkin [5] and by Ussow [6] (Fig. 1, I). Our own study of this system confirmed its general character. The components of the system react with one another and form the chemical compound $AgNO_3 \cdot KNO_3$. The binary system cadmium nitrate – silver nitrate is here investigated for the first time. The phase diagram of this system has three crystallization branches: cadmium nitrate, the compound $Cd(NO_3)_2 \cdot 2AgNO_3$ and silver nitrate. Corresponding to the maximum on the melting point curve is a melting point of 155°. The system was investigated over the range of 100 to 25% silver nitrate; at lower contents of the latter the cadmium nitrate decomposes (Fig. 1, II).

Ternary System. According to the literature sources of which we are aware, no previous study has been made of the ternary system of the nitrates of cadmium, potassium and silver.

The liquidus surface of the ternary system was investigated in 17 sections whose character and direction are shown in Fig. 2.

The melting points at the transition points of the phase diagrams of all the sections as well as the corresponding qualitative and quantitative compositions of the components are set forth in the table.

Melting Points at the Transition Points of the Ternary System and the Composition of the Components

No. of section	Equimolar percentages			Melting point at transition points
	$Cd(NO_3)_2$	KNO_3	$AgNO_3$	
I a*	58	36	6	153
I b*	36.5	59.5	4	166
II a	55	31	14	141
II b	33.5	57.5	9	158
III a	52.2	25.5	22.3	123
III b	31	55.5	13.5	147
IV a	50.2	23	26.8	115
IV b	29	55	16	146
V a	48	20	32	128
V b	45	25	30	125
V c*	27.5	54	18.5	146
VI a	46.5	15	38.5	137
VI b	39.5	28.5	32	128
VI c	25.5	53.5	21	141
VII a	49	5.5	45.5	139
VII b	41.5	4.5	54	150
VIII a	47.5	8.5	44	138
VIII b	41	7.5	51.5	150
IX a	48.5	15	36.5	132
IX b	39.5	13	47.5	149
X a	55	30	15	140
X b	45.5	24.5	30	125
X c	29	31	40	139
XI	27.3	33.7	39	132
XII a	12	40.5	47.5	124
XII b	10.5	48.5	41	128
XIII a	22.5	37.5	40	129
XIII b	18	50	32	132
XIV	36	29	35	129
XV	30.2	55.5	14.3	150
XVI a	7.8	40.5	51.7	124
XVI b	7	47.5	45.5	129
XVII a	3	46.7	50.3	131
XVII b	10.5	43	46.5	126

a* —composition and melting point of the first transition points; b* and c* —ditto of the second and third transition points respectively.

The phase diagrams of all the sections with indication of composition of starting mixtures, the course of the sections and the melting point at the transition points are shown in Figs. 3, 4, 5, 6, and 7.

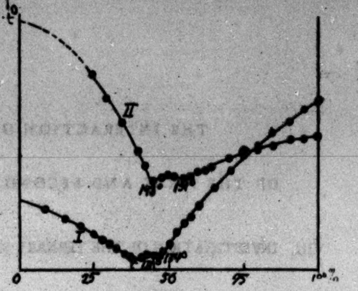

Fig. 1. Binary systems: I) $AgNO_3-KNO_3$, II) $Cd(NO_3)_2-AgNO_3$.

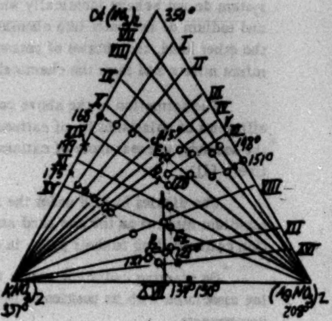

Fig. 2. Course of sections in the ternary system.

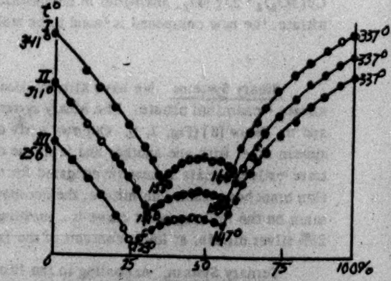

Fig. 3. Ternary sections: I) 90% $Cd(NO_3)_2$ + + 10% $AgNO_3$, II) 80% $Cd(NO_3)_2$ + 20% $AgNO_3$, III) 70% $Cd(NO_3)_2$ + 30% $AgNO_3$ in the direction to KNO_3.

The experimental data for the ternary system as a whole are generalized in the projection of the isotherms of the three-dimensional phase diagram (Fig. 8).

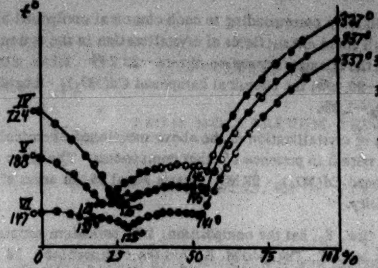

Fig. 4. Ternary sections: IV) 65% $Cd(NO_3)_2$ + 35% $AgNO_3$; V) 60% $Cd(NO_3)_2$ + 40% $AgNO_3$; VI) 55% $Cd(NO_3)_2$ + + 45% $AgNO_3$ in the direction to KNO_3.

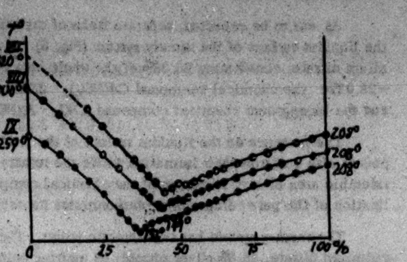

Fig. 5. Ternary sections; VII) 90% $Cd(NO_3)_2$+ + 10% KNO_3; VIII) 85% $Cd(NO_3)_2$ + 15% KNO_3, IX) 75% $Cd(NO_3)_2$ + 25% KNO_3 in the direction to $AgNO_3$.

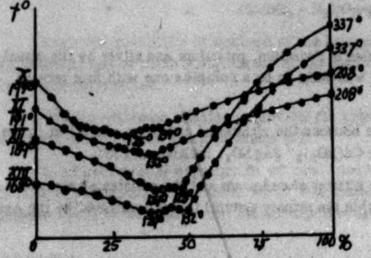

Fig. 6. Ternary Sections: X) 65% $Cd(NO_3)_2$ + + 35% KNO_3; XI) 45% $Cd(NO_3)_2$ + 55% KNO_3 in the direction to $AgNO_3$; XII) 80% $AgNO_3$ + 20% $Cd(NO_3)_2$; XIII) 65% $AgNO_3$ + 35% $Cd(NO_3)_2$ in the direction to KNO_3.

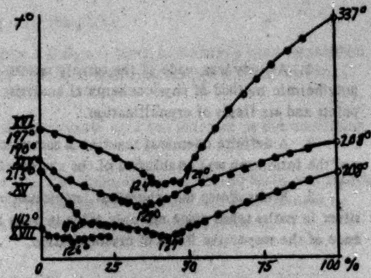

Fig. 7. XIV) 55% $Cd(NO_3)_2$+ 45% $KNO_3 \rightarrow AgNO_3$, XV) 35% $Cd(NO_3)_2$ + 65% $KNO_3 \rightarrow AgNO_3$; XVI) 87.5% $AgNO_3$ + 12.5% $Cd(NO_3)_2 \rightarrow KNO_3$; XVII) 52% $AgNO_3$ + 48% $KNO_3 \rightarrow Cd(NO_3)_2$

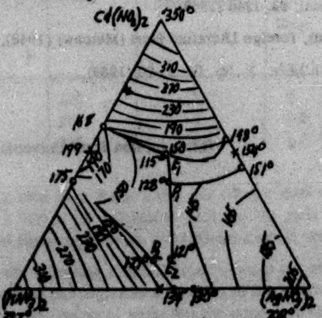
Cd(NO3)2
350°
310
270
230
190
150
170
115
E1
128°
151°
149°
199
175
130
270
230
310
E2
(KNO3)2
337
(AgNO3)2
208°

Fig. 8. Ternary system: $Cd(NO_3)_2-(KNO_3)_2-(AgNO_3)_2$

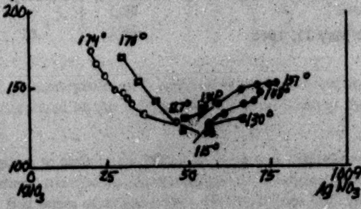

Fig. 9. Projection on to the KNO_3-AgNO_3 side.

The ternary system of the nitrates of cadmium, potassium and silver is a complex system. Its distinguishing feature is that pairs of its components: $Cd(NO_3)_2-KNO_3$, $Cd(NO_3)_2-AgNO_3$ and KNO_3-AgNO_3 react chemically and form the above-noted chemical compounds: $Cd(NO_3)_2 \cdot 2KNO_3$, $Cd(NO_3)_2 \cdot 2AgNO_3$ and $KNO_3 \cdot AgNO_3$.

As was to be expected, separate fields of crystallization corresponding to each chemical compound appear on the liquidus surface of the ternary system (Fig. 8). In all there are six fields of crystallization in the system: cadmium nitrate, constituting 23.36% of the whole area of the triangle; potassium nitrate –22.24%: silver nitrate – –28.07%: the chemical compound $Cd(NO_3)_2 \cdot 2KNO_3$–20.29%; the chemical compound $Cd(NO_3)_2 \cdot 2AgNO_3$–4.5%; and the incongruent chemical compound $KNO_3 \cdot AgNO_3$–1.6%.

The presence on the liquidus surface of the fields of crystallization of the above-mentioned chemical compounds also confirms their formation inside the ternary system in presence of other components. The quite considerable area of crystallization of the chemical compound $Cd(NO_3)_2 \cdot 2KNO_3$, nearly equal to the areas of crystallization of the pure components–demonstrates its stability.

The ternary system has two eutectic points. The first, E_1, has the composition: 23% potassium nitrate, 50.2% cadmium nitrate, 26.8% silver nitrate; its melting point is 115°. The second, E_2, has the composition: 10.5% cadmium nitrate, 48% silver nitrate and 41.5% potassium nitrate; its melting point is 121°. There are also two peritectic points: P_1 with the composition 28.5% potassium nitrate, 39.5% cadmium nitrate and 32% silver nitrate (melting point 128°): P_2 with 10% cadmium nitrate, 42% silver nitrate and 48% potassium nitrate (melting point 127°).

The orthogonal projection of the courses of crystallization onto the potassium nitrate–silver nitrate side is shown in Fig. 9.

SUMMARY

1. A study was made of the ternary system of the nitrates of cadmium, potassium and silver by the visual-polythermic method of physicochemical analysis; the system was found to be a complex one with four ternary points and six fields of crystallization.

2. A definite chemical reaction is shown to take place between the nitrates of cadmium and silver in melts and the formation was established of the chemical compound $Cd(NO_3)_2 \cdot 2AgNO_3$, melting at 155°.

3. It was shown that chemical interaction between the nitrates of cadmium and the nitrates of potassium and silver in melts takes place not only when in pairs but also within the ternary system; this is confirmed by the existence of the respective fields of crystallization.

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THE PREPARATION OF SILICOMOLYBDIC ACID FROM MOLYBDENUM TRIOXIDE AND SILICIC ACID

E. A. Nikitina, G. N. Pyatnitskaya and I. I. Angelov

The preparation of silicomolybdic acid with purification of the preparation via the etherate was proposed in a paper by one of us [1]. Although it was possible by the proposed method to obtain a pure heteropoly acid, working with such a volatile solvent as ether creates definite complications. We therefore set ourselves the task of developing a method of preparation of silicomolybdic acid which would not involve extraction with ether.

The method involved essentially a reaction between molybdenum trioxide and silicic acid in presence of water as first suggested by E. A. Nikitina [1]:

$$12MoO_3 + H_2SiO_3 + nH_2O \rightleftharpoons H_8[Si(Mo_2O_7)_6].$$

Since the possibility of synthesis of the heteropoly acid from H_2SiO_3 and MoO_3 had already been established, our problem was to make a close study of the conditions in which the above-indicated process of complex formation could be realized.

The molybdenum trioxide needed for the preparation of silicomolybdic acid was obtained in the conditions described in one of our previous papers [2].

In a first series of experiments we conducted the reaction with stoichiometric quantities of MoO_3 and H_2SiO_3; heating of the reaction mixture to 90-95° was continued for 16 hours; the volume of water was kept constant by periodic addition of fresh water; all the experiments were performed with constant stirring (Table 1).

TABLE 1

Preparation of Silicomolybdic Acid with Calculated Amounts of Molybdenum Trioxide and Silicic Acid with a 1:6 Ratio Between MoO_3 and SiO_2

No. of Experiment	Taken for synthesis (in g)		H_2O (in liters)	Duration of heating (hrs)	Sp. gr. of the obtained solution of heteropoly acid at 15°	Amt. of silicomolybdic acid obtained		Yield of MoO_3 (%)	
	MoO_3	H_2SiO_3 calculated as SiO_2				hydrated (in g)	anhydrous (in g)	on the MoO_3 taken	on the reacted MoO_3
1	500	18	3	14	1.06	144	108	20.4	63
2	250	9	1.5	14	1.06	58	44	16.6	73
3	250	9	1.5	18	1.06	66	50	19.6	83

It is seen from Table 1 that the average yield of silicomolybdic acid, calculated on the reacted molybdenum trioxide, is 73% of the calculated yield; but the yield calculated on the molybdenum trioxide taken in the reaction is low and has a mean value of 18.8% for a single boil.

In the following series of experiments it was required to observe the effect of increasing concentration of silicic acid on the degree of utilization of the molybdenum trioxide during the process of formation of the heteropoly acid; the amount of water was the same as in the first series of experiments. Results are set forth in Table 2.

The experimental results show that an increase in the silicic acid concentration raises the amount of molybdenum trioxide utilized in the reaction of complex formation, due to which the yield of heteropoly acid is also appreciably increased.

Table 2
Synthesis of Silicomolybdic Acid Using Increased Concentration of Silicic Acid (Duration of Heating 16 Hours)

No. of Experiment	Taken for synthesis		H_2O (liters)	MoO_3/SiO_2 ratio	Amount of silicic acid obtained (in g)		Yield on MoO_3 (%)	
	MoO_3 (in g)	H_2SiO_3 calculated as SiO_2 with excess (in %) of			hydrated (in g)	anhydrous (in g)	taken	reacted
1	350	50	3	1 : 8.5	80	60	17	73
2	100	100	0.8	1 : 8	22	–	20	–
3	500	500	4	1 : 8	260	200	37.7	100
4	200	500	2	1 : 10	90	70	33	87

A study was also made of the effect of change of dilution on the reaction of formation of the heteropoly acid.

In a first experiment the proportions of molybdenum trioxide and silicic acid were in accordance with the equation; the volume of water was reduced to 150 ml. The yield of silicomolybdic acid was 10% on the molybdenum trioxide taken for the reaction; the ratio between MoO_3 taken and H_2O was 1:1.4. In the second experiment, keeping the amounts of starting substances the same, the water was increased to give a MoO_3/H_2O ratio of 1:55; this raised the yield of silicomolybdic acid, reckoned on the MoO_3 taken, to 16%. Further experiments were therefore performed with increased volumes of water; at the same time the amount of silicic acid was increased in accordance with the results of the second series of experiments.

This change in the experimental conditions increased the utilization of the molybdenum trioxide taken in the reaction to 50-80%. Results are set forth in Table 3.

Table 3
Preparation of Silicomolybdic Acid in Dependence on the Degree of Dilution and the Concentration of Silicic Acid

No. of Experiment	Taken for synthesis		Excess SiO_2 (%)	H_2O (in l)	MoO_3/H_2O ratio	Duration of heating (hrs.)	Amount of silicic acid obtained (g)		Yield on MoO_3 (%)	
	MoO_3 (in g)	H_2SiO_3 calculated as SiO_2 (in g)					Hydrated	anhydrous	On MoO_3 taken	On reacted MoO_3
1	95	13	400	1.8	1:18	19	70	52	29.9	8
2	100	20	550	2.7	1:27	16	110	85	80	100
3	200	40	550	3.5	1:17	16	137	103	50	96

Having established the effect of dilution and of increased silicic acid concentration on the process of complex formation, we directed our attention to the effect of the duration of heating of the reaction mixture on the yield of heteropoly acid.

For this purpose we performed experiments with less lengthy (up to 8 hours) heating of the reaction mixture. These were performed side by side with control experiments in which the duration of boiling was 16 hours.

Results of these runs are set forth in Table 4.

TABLE 4
Effect of Duration of Boiling on the Yield of Silicomolybdic Acid: 500% Excess of H_2SiO_3 Reckoned as SiO_2

No. of Experiment	MoO_3: H_2O	Yield on MoO_3 (%)		Experiment		Duration of boiling (hours)
		MoO_3 taken	Reacted MoO_3			
1	1:18	40	75	Actual		8
2	1:18	49.9	84		Control	16
3	1:27	42	85	Actual		8
4	1:27	80	100		Control	16

These experiments show that prolongation of heating increases the participation of molybdenum trioxide in the reaction of complex formation and thereby raises the yield of silicomolybdic acid.

The foregoing data show that complete conversion of molybdenum trioxide to silicomolybdic acid is never attained in the reaction between MoO_3 and SiO_2. In different batches varying amounts of MoO_3 remain unreacted; in our experiments the amount of reacted MoO_3 ranged from 12 to 80%.

An increased percentage of MoO_3 only enters into reaction when using a large excess (550%) SiO_2 and highly diluted solution (1:25).

High dilutions, however, greatly prolong the period of evaporation of the solutions of heteropoly acids. We therefore compromised with a mean dilution of 1:15 to 1:17 and the use of a 500% excess of SiO_2 over the amount calculated from the equation.

The residue of unreacted MoO_3 and H_2SiO_3 is used again by heating with a fresh portion of water: in so doing a favorable influence of excess H_2SiO_3, dilution of solution and duration of reaction on the degree of utilization of MoO_3 is again noted. The results of the investigation are set forth in Table 5.

TABLE 5
Results of Reheating with Water of Residual MoO_3 and H_2SiO_3 from a First Synthesis

No. of Experiment	Dry slurry taken (g)	Its content of MoO_3 (%)	H_2O taken (liters)	H_2SiO_3 added (calculated as SiO_2 (g)	Amount of hydrated silicomolybdic acid obtained (g)	Residue of dry slurry (g)
1	350	89	0.5	—	35	320
2	200	96.5	1.5	30	58	127
3	267	89	2.5	20	110	289

We see from Table 5 that the nonreacted residues of MoO_3 and H_2SiO_3 may be utilized as starting materials by adding a fresh amount of silicic acid since the dried H_2SiO_3 loses its reactivity.

Crystallization of silicomolybdic acid. The preparations of diluted solutions of silicomolybdic acid (sp. gr. 1.02-1.06) are evaporated on a water bath at 70°. Due to the high solubility of silicomolybdic acid in water, the evaporation is continued until the volume is 1/5 to 1/6 of the original.

Silicomolybdic acid separates from solution in the form of a greenish-yellow crystalline mass. The great evaporation of the solutions leads to the crystallization of a dense mass which is detached with difficulty from the walls of the crystallizer and is quite free from mother liquor. In the process of evaporation (open beaker) a slight reduction of the heteropoly anion is observed; this is counteracted by the addition of a few drops of 3% hydrogen peroxide. Evaporation may also be conducted under reduced pressure; this speeds up the removal of water and minimizes the reduction of the Mo^{VI} of the heteropoly anion.

TABLE 6
Analyses of Silicomolybdic Acid and Quality of Raw Materials

No of Preparation	Chemical compounds	MoO_3 without washing free from alkali; H_2SiO_3 contains 1% Na_2O	MoO_3 without alkali salts; H_2SiO_3 contains 0.5% Na_2O	MoO_3 free from alkalies; H_2SiO_3 contains 0.5% Na_2O. Distilled water (%)	Content of anhydrous acid calculated according to the formula
		Tap water (%)			
1	MoO_3	93.47	95.8	95.6	92.9
2	SiO_2	3.13	3.5	3.85	3
3	Na_2O	3.4	0.7	0.35	—
4	$MoO_3 \cdot SiO_2$	29.3	27.3	24.9	—

Balance of starting materials. In order to check the composition of the slurry, we carried out its analysis by distilling off the MoO_3 in the form of $MoO_3 \cdot 2HCl$ hydrochlorination of a weighed amount was effected at a temperature of about 500°. In all the analyses the amount of components (SiO_2 and MoO_3) closely agreed with the calculated amount of reacted starting substances.

Weight of slurry dried at 110°: 325 g. Analysis: SiO_2 11%, MoO_3 89%.

Raw Materials. In our experiments we made use of ammonium molybdate "pure" and "pure for analysis". The MoO_3 prepared from "pure" ammonium molybdate contained from 1 to 1.7% alkali salts (reckoned as Na_2O). The MoO_3 was freed from traces of alkali metals by washing with hot distilled water (80-90°) until a colloidal solution started to form. Washing H_2SiO_3, which has been precipitated with nitric or hydrochloric acid, until it gives a negative reaction for Cl or NO_3' is a lengthy operation. The lowest Na_2O content found after washing of freshly precipitated H_2SiO_3 was 0.5% (calculated on the SiO_2). Employment of such a silicic acid leads to a final product containing alkali salts.

Precipitation of H_2SiO_3 with carbon dioxide gives a silicic acid which is readily washed and which exhibits good reactivity. The content of non-volatile residue of alkali salts in the so-prepared H_2SiO_3 is 0.025-0.03%. Silicomolybdic acid prepared by crystallization from aqueous solutions was examined by us for its content of MoO_3, SiO_2 and alkali salts (reckoned as Na_2O); loss of water was also determined at 100° and on calcination; the analytical results for samples of the heteropoly acid are set forth in Table 6.

The obtained preparations consist of saturated silicomolybdic acid.

The above data show that the quality of the obtained silicomolybdic acid depends on the purity of the starting materials.

The water content of the prepared samples of silicomolybdic acid was determined.

Losses of water at 100° amounted to 20.0, 20.3, 16.8, and 17%. The corresponding losses of water on calcination were 4.0, 2.2, 6.4, and 5.0%.

SUMMARY

1. For the first time a method of preparation of silicomolybdic acid not using ether has been developed.

2. Conditions necessary for obtaining the heteropoly acid are: 400-500% excess of silica, a reaction period of 16 hours and a volume of water equal to 8 liters per 500 g MoO_3.

3. The yield of silicomolybdic acid in these conditions is 80-90% reckoned on the MoO_3 entering into reaction.

4. 50% of the molybdenum trioxide taken enters into reaction. The unreacted MoO_3 is reused as starting material after determination of its MoO_3 content.

5. The starting materials for this method must be of a high degree of purity since it is impossible in practice to free the heteropoly acid from water-soluble impurities by crystallization.

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POLAROGRAPHIC INVESTIGATION OF THE HYDROGENATION PROCESS. I.

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An examination of the methods used by various authors for studying the behavior of unsaturated compounds in the course of catalytic hydrogenation shows that we can subdivide them into two groups. To the first group belong methods based on the establishment of the velocities of hydrogenation of individual unsaturated compounds and on the comparison of these velocities for a series of chemically related compounds.

In the majority of cases the velocity of saturation of unsaturated compounds is measured by the volume of hydrogen which combines in unit time, or by the time required for saturation of a specified quantity of substance expressed as moles, or by the time required for addition of a specified volume of hydrogen to a given quantity of the compound, or, finally, the velocity of saturation is measured from the rate of change of some physical constant of the substance, such as the refractive index, the rotatory power, etc..

A number of authors [1-10] have employed the technique of comparing the velocities of saturation of pure compounds to draw conclusions about the effect of the structure of the molecules on the activity of the multiple bond in the process of catalytic hydrogenation. Other authors [11, 12], by hydrogenating mixtures of pure unsaturated compounds with one and the same standard substance, have compared the so-obtained partition coefficients of hydrogen and have established the effect of structural peculiarities of molecules on the reactivity of the double bond.

It has been found, however, that comparison of the rates of saturation of pure compounds, or determination of the coefficients of distribution of hydrogen between pure unsaturated compounds and the standard substance, do not permit us to draw conclusions about the behavior of these unsaturated compounds in mixtures.

The second group of methods of study of the behavior of unsaturated compounds during the hydrogenation process includes the methods of joint hydrogenation of two competing substances, of hydrogenation of binary mixtures with the aim of direct establishment of the order of hydrogenation of the components of the mixture. We must bear the following facts in mind: 1) In the vast majority of cases the experiments were run with small amounts of material (1/200 to 1/100 mole); 2) if the starting mixture contains two components, then the saturation process will lead to at least two hydrogenation products so that the binary mixture is changed into a quaternary mixture; 3) the quantitative separation of compounds, especially when they are similar in functional character, is extraordinarily difficult and in the majority of cases impossible. In order to be able to follow the whole course of the process, it would be desirable to withdraw small samples of reaction mixture at definite intervals of time and to analyze them. But if, say, one-tenth of the mixture is to be withdrawn each time, this would correspond to 1/2000 to 1/1000 mole. It would be a very difficult problem to separate such an amount into the four components for the purpose of establishing the content of each in the mixture. Very rarely, therefore, is the attempt made to effect direct analysis of a mixture at different stages of hydrogenation, and even as a rule for the purpose of evaluating the course of the process of saturation of binary mixtures, recourse is had to indirect methods. The most important of the indirect methods is that developed by S. V. Lebedev [13] which is based on the study of hydrogenation curves.

Such a method, however, does not permit the study of intermediate processes, i.e. with a not strictly maintained selectivity; in the course of the process one component of the mixture is preferentially saturated; at the same time the other component undergoes saturation although at a much lower velocity. The degree of selectivity of the process may vary widely and the hydrogenation curves do not permit us to determine the degree of selectivity.

Other workers apart from S. V. Lebedev who studied the course of hydrogenation of binary mixtures of diolefinic and acetylenic compounds on the basis of the character of the hydrogenation curves were Dupont [14], Armstrong and Hilditch [15] and Yu. S. Zalkind [16].

The marked inadequacy of the information supplied by the hydrogenation curves prompted the first investigators of problems of selectivity of hydrogenation to resort to analysis of the mixtures, using the method of interrupted hydrogenation. This method consists essentially in interrupting the hydrogenation of an equimolecular mixture of two unsaturated compounds when 50% of the theoretical amount of hydrogen has been absorbed and

and then analyzing the mixture as a whole; on the basis of the results of this analysis, conclusions are drawn about the presence or absence of selectivity and about the degree of selectivity of the process.

Of the numerous authors who utilized the method of interrupted hydrogenation, we may mention Vavon [17], Bourguel [18], Yu. S. Zalkind [16, 19], B. A. Kazansky [20] and M. I. Ushakov [9].

Different authors used different methods of analysis of the reaction mixture [21]. In all cases the procedure is quite complicated; the main defect of the method is that it characterizes the state of the process not throughout its entire course, but only at one determined moment.

It is therefore natural to search for a method which would permit the course of the process to be followed at any rate at a few points. The obvious plan is to effect direct or indirect analysis of samples withdrawn from the reaction mixture at intervals throughout the process.

Many attempts to develop a procedure along these lines have been made. We may refer to the work of Vavon [22] who followed the course of hydrogenation of limonene and carvone by withdrawing samples from the reaction mixture at intervals and measuring the angle of rotation of the plane of polarization of light.

In the study of the process of hydrogenation of fats with the objective of establishing its selectivity, Kaufmann [23] and later Zinovyev [24] successfully applied the method of determination of the iodine and thiocyanogen numbers.

V. V. Ipatyev [25] hydrogenated a mixture of allyl alcohol and oleic acid and withdrew samples over definite intervals of time; he determined the amount of stearic acid formed by precipitation with magnesium acetate and the total amount of unsaturated compounds remaining in solution from the amount of iodine chloride absorbed by them. A slightly modified procedure was employed by I. F. Bogdanov and E. I. Bashkirova [26].

Performance of an experiment in the apparatus used in the above-cited investigations [24, 26] necessitated relatively large amounts of unsaturated compounds, in addition to which the procedure for analysis of the mixtures was rather complicated. We therefore reached the following conclusions:

1. Study of the course of the hydrogenation of binary mixtures from the saturation curves (S. V. Lebedev) only gives an approximate conception of the character of the process.

2. The method of interrupted hydrogenation does not give an idea of the state of the process throughout its entire course, so that its value is seriously limited.

3. The method of withdrawal of a series of samples in the course of the process is the most interesting and informative in the sense that it permits study of the kinetics of the process. Up to now, however, the proposed methods of analysis of mixtures have been laborious, only applicable to a limited number of materials, and frequently required large amounts of substance.

In seeking for an analytical method of adequate sensitivity and accuracy, speedy and easy in use, enabling operation with very small quantities of substance, and applicable to a fairly wide range of chemical compounds, we decided on the polarographic method.

In the conditions of the investigation we were faced with the following problem: Knowing that two given unsaturated compounds are present in the mixture to be hydrogenated, and knowing also the amount of hydrogen consumed up to the instant of withdrawal of the sample from the vessel, it is desired to determine polarographically how much of each unsaturated compound is left in solution, assuming that the respective saturated compounds do not give polarograms and that their presence does not affect the polarographic behavior of the unsaturated compounds.

This problem can be solved in two ways, depending upon whether both or only one of the unsaturated components of the mixture give polarograms.

In the event that both components of the mixture give definite and separate polarographic waves, the problem is solved by plotting polarograms at different stages of hydrogenation, by measurement of the height of each wave and, insofar as the proportionality coefficient between the diffusion current and the concentration is known, by calculation of the concentration of each component in the solution. In the course of the hydrogenation reaction, either the heights of the waves of both components will gradually decrease but the change will differ for each component in dependence on the degree of selectivity of the process, or both waves will decrease to identical extents at the same time (non-selective process), or the heights will decrease simultaneously, but at different rates (one more quickly than the other—not strictly selective process), or at first only the height of one of the waves will decline and its disappearance will be followed by the start of decline of the other wave (strictly selective process).

In Figure 1 are shown curves obtained by polarographic determination of a series of specimens withdrawn during the hydrogenation of a mixture of maleic and fumaric acids; on these curves the wave at a more positive value of the potential relates to maleic acid; that at a more negative value to fumaric acid. The half-wave potential of maleic acid differs from that of fumaric acid by 0.2 V, which allows of clear demarcation of one wave from the other. Measurements of the height of the waves on the curves gave us the values set forth in Table 1.

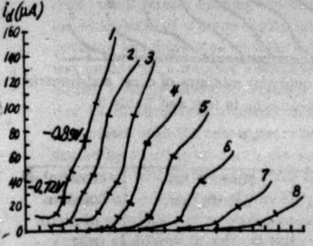

Fig. 1. Polarograms of mixtures of maleic and fumaric acids $\eta = 1/10$. Explanation in text and Table 1.

In the starting solution (specimen no. 1, Table 1) the concentrations of maleic and fumaric acid were taken as equal to:

$$C_m = C_f = 250 \cdot 10^{-5} \text{ mol/liter.}$$

We see from the data of Table 1 that maleic acid is preferentially hydrogenated in comparison with fumaric acid; the selectivity, however, is not strict since at the instant of complete disappearance of maleic acid, the fumaric acid has been partly (only to the extent of 17%) hydrogenated.

In some cases it is useful to obtain information about the concentration of the substance which is being analyzed by applying the so-called method of addition of a standard solution, which ensures greater accuracy of determination, although a longer period is then required for the determination. In the present investigation we resorted to this method in many cases.

When only one of the two components of a mixture forms a polarogram, the change of content of that compound in the course of hydrogenation can be directly determined by measurement of the height of the single wave on the polarograms of withdrawn samples; the change in content of the other component is calculated by the method explained in the example below.

Figure 2 contains a series of polarograms plotted for samples of a solution of an equimolar mixture of fumaric acid and oleic acid which had been subjected to hydrogenation; samples were taken throughout the course of the reaction at intervals corresponding to absorption of each 20-30 ml hydrogen. Only one wave changes on the polarogram — that of fumaric acid oleic acid does not give a polarographic wave. The initial concentration of fumaric acid (as also that of oleic acid) was $250 \cdot 10^{-5}$ mole/1. The heights of the waves of all nine curves in Figure 2 and the corresponding concentrations of fumaric acid are set forth in Table 2.

TABLE 1

No. of samples on curves	Height of wave (mm)		Maleic acid $C \cdot 10^{-5}$	Fumaric acid $C \cdot 10^{-5}$
	Maleic acid	Fumaric acid		
1	405	660	250	250
2	270	660	167	250
3	190	620	117	235
4	120	600	74	227
5	0	545	0	207
6	0	352.5	0	134
7	0	140	0	53
8	0	70	0	26

In the experimental conditions of the experiment which we describe as an example, the saturation of the weighed amounts of fumaric and oleic acids (each 0.005 g/mole) should have required 246.2 ml hydrogen (at an air temperature of 14° and a barometric pressure of 727 mm). Such an absorption should correspond to a fall in the concentration of each of the acids, in the solutions diluted for polarogramming, from $250 \cdot 10^{-5}$ mole/$\underline{1}$ to nil. Assuming, for convenience, $1 \cdot 10^{-5}$ mole/$\underline{1}$ as unit of concentration, we may say that the concentration of each acid in these arbitrary units before the start of hydrogenation was 250 (total 500) and that after completion of hydrogenation it was 0. Hence the fall in concentration for each arbitrary unit corresponds to a hydrogen absorption of $\frac{246.2}{500} = 0.4924$ ml.

The amount of hydrogen absorbed up to the instant of withdrawal of each of the samples is known from the readings of the gas burets; we must, however, introduce a correction into these readings; on withdrawing a sample of solution for analysis, we change each time the absolute weight of unsaturated compounds participating in the reaction. In the experiment we are now considering, the first sample was taken before the start of hydrogenation; samples 2 to 8 were each taken after absorption of 20.0 ml hydrogen; sample 9 was taken after absorption of 29.2 ml hydrogen. The volume of each sample was 2 ml while that of the original solution was 40 ml. The volumes of hydrogen which would have been absorbed by the original amount of material at the instant of withdrawal of the samples are shown in Table 3, from which we see how the volumes were calculated.

TABLE 2

No. of sample and curve	Height of fumaric acid wave	Fumaric acid $C\cdot10^{-5}$
1	370	250
2	350	236
3	310	209
4	280	189
5	240	162
6	170	115
7	110	74
8	67	45
9	0	0

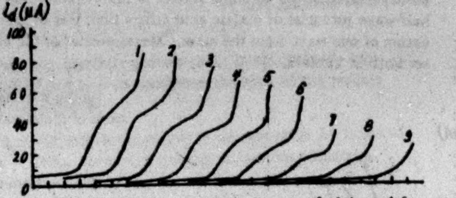

Fig. 2. Polarograms of equimolar mixtures of oleic and fumaric acids. η = 1/10. Explanation in text and Table 2.

TABLE 3

No. of sample	Hydrogen absorbed (in ml)	Vol. of solution (in ml)	Formula for calculation	Total absorption of H_2 (in ml)
1	0	40	—	0
2	20	38	$\frac{20\cdot40}{38}$	21.1
3	20	36	$21.1+\frac{20\cdot40}{36}$	43.3
4	20	34	$43.3+\frac{20\cdot40}{34}$	66.8
5	20	32	$66.8+\frac{20\cdot40}{32}$	91.8
6	20	30	$91.8+\frac{20\cdot40}{30}$	118.5
7	20	28	$118.5+\frac{20\cdot40}{28}$	147.1
8	20	26	$147.1+\frac{20\cdot40}{26}$	177.9
9	29.2	24	$177.9+\frac{29.2\cdot40}{24}$	226.5

Knowing the fall in concentration of fumaric acid at the instant of withdrawal of each sample, we calculate how much hydrogen was consumed in saturating this acid by multiplying the fall in concentration ΔC by 0.4924; the difference between the total absorption and the absorption by fumaric acid corresponds to the absorption of hydrogen by oleic acid; on dividing this difference by 0.4924, we obtain the fall in oleic concentration at the instant of withdrawal of a sample

This calculation is illustrated for a specific example in Table 4.

Consequently, in this case also, when only one of the two unsaturated components forms a polarogram, we still have the possibility of sufficiently accurately tracing the change of concentration of both components in the course of hydrogenation.

On the basis of the foregoing observations, we arrive at the conclusion that polarography enables us to follow the course of joint hydrogenation of two unsaturated compounds either when the respective saturated compounds do not give polarographic waves (as is mostly the case), or when both unsaturated compounds give sharply separated waves, or only one of the two compounds gives a polarographic wave. Experiment showed that by varying the conditions of polarography (the nature of the solvent and the pH) it is nearly always possible to an adequate extent to separate the waves of the two unsaturated compounds or to suppress one of the waves.

TABLE 4

No. of sample	Fumaric acid		Total H_2 absorption (ml)	Distribution of H_2 over		Oleic acid	
	$C\cdot10^{-5}$	$\Delta C\cdot10^{-5}$		Fumaric acid	Oleic acid	$\Delta C\cdot10^{-5}$	$C\cdot10^{-5}$
1	250	0	0	0	0	0	250
2	236	14	21.1	6.9	14.2	29	221
3	209	41	43.3	20.2	23.1	47	203
4	189	61	66.8	30.0	36.8	75	175
5	162	88	91.8	43.3	48.5	98	152
6	115	135	118.5	66.5	52.0	106	144
7	74	176	147.1	86.7	60.4	123	127
8	45	205	177.9	100.9	77.0	156	94
9	0	250	226.5	123.1	103.4	210	40

Consequently the polarographic method of investigation is only unsuitable in cases when both unsaturated compounds do not give polarograms or when the two waves coincide or have similar reduction potentials in all the conditions of polarogramming.

Our apparatus for carrying out hydrogenations most closely resembled that of S. V. Lebedev [27] and different in minor details.

The hydrogenation vessel is a duck and differs from the normal type in the presence, apart from two openings with taps of which one serves for connecting the hydrogen buret and the other for connection to atmosphere, of a third, small lateral opening which can be tightly closed by means of a tautened rubber cap; this opening is intended for withdrawal of samples during hydrogenation. The duck was rocked 300, 225 and 150 times per minute. Hydrogenation was performed with the catalyst prepared by A. S. Ginzberg's method [28]. Through the sampling opening was introduced a weighed amount of aluminum or nickel powder; the particles of metal were washed off with 5 ml solvent (usually alcohol). Through the same opening with a pipet was introduced, depending on the circumstances, 5 or 10 ml aqueous or alcoholic solution of $PtCl_4$ or Na_2PdCl_4 of predetermined concentration. The opening was then closed with the rubber cap, the duck secured in the frame of the shaker, immersed in a thermostat and connected by a rubber tube with the hydrogen line. The experimental temperature was 25 or 40°. Through the duck was passed 500 ml hydrogen, the tap was closed, and the duck connected to atmosphere; with the help of a medicinal syringe – by means of which the rubber cap is punctured – a solution of 1/200 to 1/100 g/mole of the substances or mixture of substance to be hydrogenated is introduced; with the same syringe is also introduced a small amount of solvent in order to bring the total volume of liquid to 40 ml. After the hydrogen in the buret has been levelled to atmospheric pressure, the shaker is started and reading is started of the amount of absorbed hydrogen every 60 seconds with the help of a timing device.

Samples are withdrawn in the following way: The shaker is stopped, the cap is punctured with the needle of a syringe, 2 ml is aspirated from the duck, and the shaker is again started. The sample is transferred to a vessel from which exactly 1 ml is withdrawn with a pipet, transferred to a moistened filter for separation of the catalyst, and repeatedly washed with the solution serving as the medium for the subsequent polarographic analysis; the volume of the filtrate is made up with the same solution to 25 ml or, more often, to 50 ml.

The first sample is withdrawn before the start of hydrogenation, the subsequent samples are taken off after each 20 ml of absorbed hydrogen.

The polarographic analysis was performed with the A-3 polarograph and with the M-7 visual polarograph. The comparison electrode was a saturated calomel electrode.

SUMMARY

1. For the purpose of investigating the selectivity characteristics in the course of hydrogenation of mixtures of unsaturated compounds, the method of polarographic analysis of samples withdrawn during the hydrogenation is proposed.

2. It is shown that the polarographic method is suitable when both components of the mixture give clearly resolved waves and also when one of the two unsaturated compounds gives a polarographic wave and the other does not give a wave.

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A SYSTEM WITH AN ENCLOSED REGION OF STRATIFICATION

THE RECIPROCAL SOLUBILITY OF HEXAMETHYLENEIMINE AND WATER

E. N. Zilberman and Z. D. Skorikova

At the present time the general assumption is that the usual form of solubility curve of binary systems is a closed ring [1]. In the majority of systems, however, it is impossible to observe either upper or lower critical points. It is especially rarely that we encounter systems with a lower critical point. This circumstance is usually explained by the onset of crystallization [1]. The few systems with a lower critical temperature which have been studied are characterized by the formation of chemical compounds which (as illustrated by R. V. Mertslin [2] with reference to mixtures of water and some amines) break down into their original constituents on heating so that stratification of the homogeneous solutions takes place. Due to the strong attraction between different types of molecules at low temperatures, the components of chemically interacting binary systems form homogeneous solutions. With rising temperature, the possibility of development of heterogeneous mixtures arises at the same time as decomposition of the associated, solvated or other types of compounds.

We have studied the reciprocal solubility of hexamethyleneimine and water. As had been expected, in the light of the foregoing considerations, notwithstanding the complete reciprocal solubility of the two substances at room temperature [3], a lower critical point was observed in the system hexamethyleneimine-water. We also succeeded in demarcating both branches of the solubility curve and in finding the position of the upper critical point.

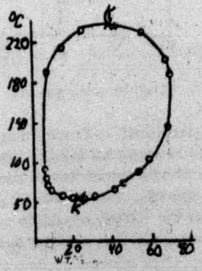
EXPERIMENTAL

The hexamethyleneimine whose constants had been previously determined [3] was used in the experiments. Solubility was determined by the polythermal method of V. F. Alekseev [4], based on the appearance and disappearance of turbidity on slow heating of mixtures of determined composition in sealed tubes.

The curve of reciprocal solubility of hexamethyleneimine and water (see diagram) was plotted on the basis of the experiments performed. Interpolated data are set forth in the table.

TABLE 1
Reciprocal Solubility of Hexamethyleneimine and Water

Temperature (in °)	Content of hexamethyleneimine in mixture (wt. %)	
	in upper layer	in lower layer
66.9*	22.5	22.5
70	36.8	10.0
80	49.6	6.8
90	57.5	5.8
100	62.4	5.7
110	65.5	5.7
120	67.5	5.7
130	68.9	5.7
140-160	70.3	5.7
170	70.3	5.8
180	70.3	6.0
190	70.0	6.8
200**	68.0	9.8
210	62.5	15.5
220	53.0	23.9
228*	39.5	39.5



Curve of reciprocal solubility of hexamethyleneimine and water. K – critical points.

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*Critical temperature.

**On heating above 200° the contents of the tubes turned yellow.

The lower critical temperature (found to be 66.9°) was determined experimentally. Critical opalescence was observed at this temperature. The upper critical temperature is 228° and was obtained by graphical extrapolation by extending the line joining the center of the connecting straight lines up to the point of its intersection with the solubility curve.

Since the system hexamethyleneimine-water has both an upper and a lower critical temperature, both branches of the solubility curve are characterized by the presence of "minimum solubility", i.e. points (or, in our case, sections) above and below which the solubility rises.

SUMMARY

1. It is shown that the system hexamethyleneimine-water possesses both a lower and an upper critical temperature. Corresponding to the lower critical temperature (66.9°) is a mixture containing 22.5 wt. % hexamethyleneimine; corresponding to the upper critical temperature (228°) is one containing 39.5 wt.% hexamethyleneimine.

2. The minimum of solubility of hexamethyleneimine in water occurs at 100-160° and is 5.7%. The minimum solubility of water in hexamethyleneimine is 29.7% and is observed over a very broad temperature range (140-180°).

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MELTING POINTS AND POLYMORPHIC TRANSFORMATIONS OF THE HYDROXIDES OF LITHIUM, SODIUM AND POTASSIUM

V. A. Khitrov, N. N. Khitrova and V. F. Khmelkov

It is usually assumed that the melting point of lithium hydroxide is 445°, that of sodium hydroxide 318.4° and that of potassium hydroxide 360° [1]. Being engaged over a period of years in the study of the interaction of hydroxides of alkali metals with salts in melts, we were naturally forced to pay attention to the purity of our preparations and, in particular, to the purity of the alkalies. We prepared the purest NaOH and KOH, on A. G. Bergman's suggestion, from chemically pure metals (Kahlbaum), in a silver beaker under a glass bell, by the action on these metals of twice-distilled water in an atmosphere of hydrogen followed by dehydration at about 500° in a furnace constantly filled with air from which carbon dioxide and water vapor had been completely removed (by passage through two Tishchenko bottles containing sulfuric acid and three columns filled with small lumps of KOH). Analysis of the NaOH and KOH prepared by this method showed that they contain only traces of moisture and carbonates; their melting points were respectively 322 and 406° [2].

The melting points of the caustic alkalies were measured in a specially designed muffle furnace [2] filled with air free from carbon dioxide and water vapor. Measurement was effected with a nichrome-constantan or gold-platinum thermocouple whose hot junction was directly immersed in the alkali melt. The scale of the millivoltmeter was graduated on the basis of the boiling point of water and the melting point of chemically pure metals (tin, lead and zinc). The alkalies were melted in silver crucibles. The thoroughness of the protection of the alkali melt against the surrounding air in our procedure is evident from the fact that the melting point of the alkali melts remained substantially unchanged even after a residence time of 10 hours in the furnace.

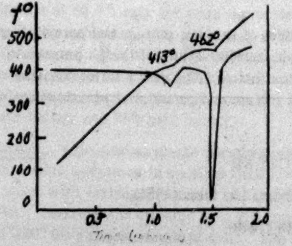

Fig. 1. Heating curve of LiOH

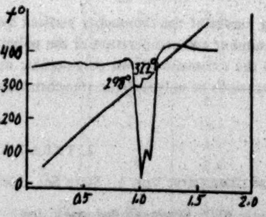

Fig. 2. Heating curve of NaOH

We also obtained good results in the purification of chemically pure hydroxides (Umformer, Merck and Kahlbaum grades) by Sörensen's method [3], involving standing for many days of the saturated aqueous solutions followed by careful dehydration for 6 hours in an atmosphere freed from carbon dioxide and water vapor. Our results were sufficiently good: melting point of NaOH 320-321°, of KOH 403-404°, of LiOH 462-463°. We thought it necessary to check the data for the melting points of the hydroxides of lithium, sodium and potassium against the heating curves of specimens purified by one of the above-mentioned methods. For this purpose we used the pyrometer of N. S. Kurnakov and a differential recorder.

The hot junction of the nichrome-constantan thermocouple was directly immersed in the alkali melt. This thermocouple had been graduated against the boiling point of water and the melting points of chemically pure tin, lead and zinc. The alkali melt was contained in a silver crucible placed in a stout silver block. The alkali was melted in a furnace constantly filled with air from which carbon dioxide and water vapor had been removed. The thermocouple was mounted in the massive silver cover of the crucible. In this set-up the block was rapidly cooled with liquid oxygen contained in an aluminum vessel the air in which was free from carbon dioxide and water vapor. The block was transferred to the furnace and the heating curve was plotted. Programmed temperature regulation was effected according to the scheme proposed by V. I. Kaurkovsky [4] with the help of a potential regulator for which a thyratron relay served as the impulse element.

The plotted curves (Figs. 1 to 3) confirmed our data and we can now confirm that the melting points are LiOH 462°, NaOH 322° and KOH 406°.

Repeated recordings of the heating curves of the hydroxides of lithium, sodium and potassium also gave information about the number and temperatures of the polymorphic transformations of these compounds. We could establish the presence in LiOH of a polymorphic transformation which, as far as we know, has not previously been reported. Transition of the α-modification of LiOH into the β-form takes place at 413° (Fig. 1).

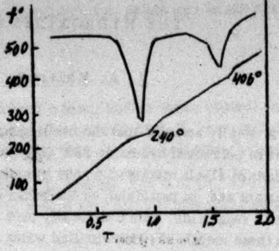

Fig. 3. Heating curve of KOH

The transition from one modification of NaOH into the other occurs at 298°. It is very interesting to note that the endothermic effect of the polymorphic transformation of NaOH is very much larger than the melting effect. This is undoubtedly bound up with the fact that both effects occur at almost identical temperatures (Fig. 2). Contrary to the statement of N. A. Reshetnikov and G. G. Diogenov [5], who found three polymorphic modifications of KOH with transformation temperatures of 258 and 375°, our repeated and highly concordant checks revealed only one extremely marked endothermic effect at 240°, corresponding to the transformation of the α-modification of KOH into its β-form (Fig. 3). As in the case of NaOH, the effect of the polymorphic transformation of KOH was much more conspicuous than the melting effect.

T. A. Polivanova collaborated in the research and the authors extend their thanks to her.

SUMMARY

1. Carefully purified hydroxides of lithium, sodium and potassium have higher melting points than those recorded in the handbook literature.

The following melting points were established by visual and thermographic investigation: lithium hydroxide 462°; sodium hydroxide 322°; potassium hydroxide 406°.

2. The heating curves of the thoroughly purified hydroxides of lithium, sodium and potassium permit the establishment of the number and temperature of the polymorphic transformations of these compounds. For the first time we established the existence of two polymorphic modifications of LiOH with a transformation temperature of 413°. The temperatures of polymorphic transformations of sodium and potassium hydroxides are respectively 298 and 240°.

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THERMOCATALYTIC TRANSFORMATIONS OF HYDROCARBONS

IV. TRANSFORMATIONS OF DIPHENYLETHANE AND DITOLYLETHANE

A. F. Dobryansky, L. A. Ponomarev and L. D. Dybkin

As a development of work on the transformation of diphenylmethane [1], studies were made of the decomposition of diphenylethane and ditolylethane. As we know, the first of these hydrocarbons forms toluene and complex condensation products on pyrolysis. In precisely the same way ditolylethane forms dimethylbenzene and analogous condensation products. However, whereas diphenylethane forms only toluene, ditolylethane gives, apart from the anticipated dimethylbenzene, an appreciable amount of toluene. This reaction also occurs appreciably in catalytic decomposition with anhydrous aluminum chloride, the action of the latter being quite sililar to that of aluminosilicates. It had been expected that on heating with aluminosilicate catalyst the indicated course of reaction would be even more marked.

EXPERIMENTAL

Diphenylethane was synthesized from benzene and dichloroethane in presence of aluminum chloride. The best yields were obtained with a large excess of benzene (100 parts dichloroethane, 900 parts benzene and 6 parts aluminum chloride), a duration of reaction of 6 hours, and heating on the water bath to 90° (at the end of the reaction). In these conditions the yield was about 70%.

Ditolylethane was synthesized on precisely similar lines; with a large excess of toluene, the yield rose to 80% of the theoretical. Solid diphenylethane was purified by distillation and by crystallization from alcohol (m.p. 52°). Ditolylethane was purified by distillation; the 290-300° fraction was collected. The ortho-isomer melted at 82°, the para-isomer at 66.5°; only the meta-isomer is a liquid. We obtained a substance with a viscosity at 20° of 7.6815 centistokes and d_4^{20} 0.9677, n_D^{20} 1.5750. Judging by the relative yields of phthalic acids obtained on oxidation with potassium permanganate, this substance is a mixture of 72% meta-isomer and 28% para-isomer.

Diphenylethane. Experiments on the transformation of diphenylethane were performed in standard conditions, i.e. in an iron retort with activated gumbrin as catalyst, using a 1:1 ratio.. Heating was effected over a burner at 170, 180 and 190° for various periods of time. The temperature was measured with a thermometer immersed in the reaction mixture. After expiration of a determined period, the mixture was cooled and a sample of the liquid was withdrawn for analysis for its benzene content.

Fractionation gave the following yields of benzene in dependence on the duration of heating (Table 1).

TABLE 1

Yield of Benzene in the Transformation of Diphenylethane

Temp. (in °C)	Duration of heating (in hours)	Yield of Benzene (in %)
170	4	0.5
	9	2.1
	10	2.3
	20	2.9
	30	3.1
	40	3.1
180	1.5	1.2
	4	2.3
	8	3.6
	10	3.8
	20	4.6
	35	4.7
190	1	3.8
	4	6.0
	7	9.7
	10	12.2
	15	14.5
	18	15.0
	26	15.0

In all cases pure benzene was obtained: d_4^{20} 0.8790, n_D^{20} 1.5012. Distillation in vacuum (4 mm) of the higher products gave fractions boiling at 200-260° and 270-290°. The latter fraction markedly predominated. Analysis of the first of the high-boiling fractions showed that it consists of undecomposed diphenylethane contaminated with higher products of reaction.

Analysis of the second fraction.

Found %: C 92.11; H 7.79; M 279. Diphenethylbenzene $C_{22}H_{22}$. Calculated %: C 92.30; H 7.70; M 286.

Oxidation of the second fraction with potassium permanganate gave (from 5 g hydrocarbon) 1.5 g benzoic acid and 1.6 terephthalic acid. The benzoic acid melted at 121°; the content of COOH was determined by titration and found to be 36.59 (calculated 36.88%). The terephthalic acid melted at about 310° in a sealed tube; neutralization with KOH gave a COOH content of 53.17 and 53.44 compared with the calculated amount of 54.2%.

All these data permit us to represent the catalytic transformation by the following equation:

$$2C_6H_5CH_2CH_2C_6H_5 = C_6H_6 + C_6H_5CH_2CH_2C_6H_4CH_2CH_2C_6H_5.$$

The transformation scheme in no way differs from the usual scheme for thermocatalytic transformation of alkylbenzenes.

In addition to the above-described reaction products, the higher fractions contained a more complex hydrocarbon, evidently formed with four phenyl groups linked by $-CH_2CH_2-$ groups.

TABLE 2

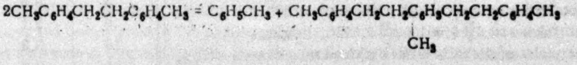
Ratio of Amounts of Toluene and Dimethylbenzene in Dependence on the Weight of Catalyst

Ditolylethane (g)	Catalyst (g)	Toluene (g)	Dimethylbenzene (g)	Ratio of toluene yield to dimethylbenzene yield
100	200	15.8	7.7	2.3
100	100	14.7	7.4	2.3
100	50	12.5	6.6	2.1

Ditolylethane. Three experiments were run with ditolylethane in the same conditions as with diphenylethane. In the third experiment were used 200 g catalyst (activated gumbrin) and 100 g ditolylethane. Fractionation of the products of transformation gave: 107-112°, 1.96 g; 112-134°, 2.1 g; 134-142°, 5.2 g; 142-160°, 1.9 g; 160-170°, 4.6 g; 170-330°, 21.0 g; above 330°, 35.9 g; losses 9.7 g.

The 107-112° fraction is mainly toluene, d_4^{20} 0.863. The 112-134° fraction is a mixture of toluene and xylene and was subsequently found to consist of equal parts of these hydrocarbons; similarly the 142-160° fraction was resolved into xylene and trimethylbenzene. The 134-142° fraction was xylene with d_4^{20} 0.862. Judging by the structure of the original ditolylethane, the latter fraction would be a mixture of m- and p-xylenes.

For the toluene type of transformation according to the equation



$$2CH_3C_6H_4CH_2CH_2C_6H_4CH_3 = C_6H_5CH_3 + CH_3C_6H_4CH_2CH_2\underset{\displaystyle CH_3}{\underset{|}{C_6H_3}}CH_2CH_2C_6H_4CH_3$$

the yield of toluene must amount to 47.1% of the theoretical yield. By analogy, for the xylene transformation the yield of xylene must be 25.2%. In practice the ratio of toluene to xylene is much higher; instead of 1.87:1 it is 4:1; hence it follows that the toluene decomposition must be regarded as the main reaction.

With progressive transformation of the ditolylethane heated with catalyst to a maximum temperature of 350°, the yield of distillate was 65% (calculated on the charge of raw material) in experiments with distillation of the reaction products. The ratio of the toluene to dimethylbenzene formed was substantially constant (Table 2).

In experiments with decomposition under a reflux condenser, when the formed reaction products were able to react for a long period with the catalyst, the ratio of toluene to dimethylbenzene was as high as 4:1. From this we can conclude that the dimethylbenzene formed itself participates in the further transformations with formation of methyl- and trimethylbenzene, as we had previously shown [2].

SUMMARY

1. Transformation of diphenylmethane in presence of aluminosilicate catalyst leads to formation of benzene alone in the volatile fraction.

2. Transformation of ditolylethane leads to initial formation of toluene and dimethylbenzene at the same time; increasing duration of contact with the catalyst increases the proportion of toluene due to secondary changes of the dimethylbenzene.

3. Formation of benzene from diphenylethane has an equilibrium character which is governed by the temperature.

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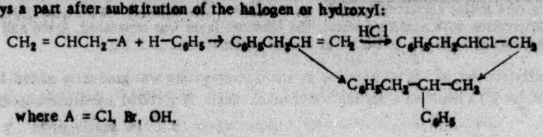
*See Consultants Bureau Translation, page 1535.

CONDENSATION OF ALLYLACETATE WITH BENZENE IN PRESENCE OF $AlCl_3$

I. P. Tsukervanik and S. G. Melkanovitskaya

Many authors have studied the condensations of allyl halides and allyl alcohol with benzene in presence of acid catalysts. Formation of 1,2-diphenylpropane has been observed in the majority of cases. In some cases, however, it was possible to isolate products containing one phenyl group. Nenitzesku [1] obtained 2-chloropropylbenzene together with 1,2-diphenylpropane from allyl chloride and benzene in presence of $FeCl_3$ and $ZnCl_2$. In our laboratory [2] allylbenzene and 2-chloropropylbenzene were obtained with the same catalyst and allyl alcohol. Allylbenzene was also obtained in low yields when using BF_3 [3], HF [4] and $AlCl_3$ [5]. In a recent paper Losev and co-workers [6] showed that condensations of allyl chloride in presence of $AlCl_3$ proceed in the first place with reaction of the chlorine atom, and the formed allylbenzene is subjected to various transformations. Consequently the literature data indicate that in the reactions discussed the double bond of allyl compounds only plays a part after substitution of the halogen or hydroxyl:



$$CH_2=CHCH_2{-}A + H{-}C_6H_5 \rightarrow C_6H_5CH_2CH=CH_2 \xrightarrow{HCl} C_6H_5CH_2CHCl{-}CH_3$$

$$\rightarrow C_6H_5CH_2{-}\underset{C_6H_5}{CH}{-}CH_3$$

where A = Cl, Br, OH.

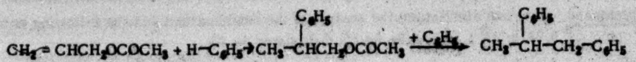
Some condensations of allyl bromide and allyl chloride with benzene in presence of H_2SO_4 and HF have been described, however, which proceed only at the double bond [7].

We must also bear in mind that in certain specific conditions the condensations may lead almost entirely to anomalous products. Long ago the case was described of preparation from allyl chloride and benzene of propylbenzene in high yield [8].

We have studied the reaction of allylacetate with benzene with the aim of ascertaining whether addition at the double bond is possible.

The condensations of vinylacetate with benzene described by Korshak and co-workers [9] lead to acetophenone, 1,1-diphenylethane and 9,10-dimethyldihydroanthracene. Under the influence of $AlCl_3$ the first step is evidently cleavage of the ester linkage of vinyl acetate. On the other hand in our laboratory [10] it was possible in mild conditions to realize the normal condensation of vinylbutyl ether with benzene. One patent [11] claims the preparation of various β-phenyl compounds by condensation of vinyl derivatives (including vinyl acetate) with aromatic hydrocarbons in presence of $AlCl_3$.

It was to be expected that the great distance of the double bond from the ester group in allylacetate would cause the latter to react, if only partly, according to the following scheme:



$$CH_2=CHCH_2OCOCH_3 + H{-}C_6H_5 \rightarrow CH_3{-}\overset{C_6H_5}{C}HCH_2OCOCH_3 \xrightarrow{+C_6H_6} CH_3{-}\overset{C_6H_5}{CH}{-}CH_2{-}C_6H_5$$

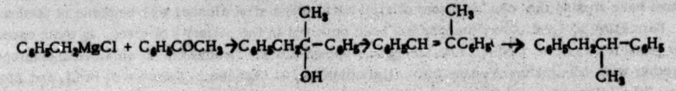
We started our study of the reactions by using small quantities of $AlCl_3$, but it was found that condensations do not then take place either in the cold or with heating. Only when using a slight excess of $AlCl_3$ over the equimolar amount (1.1 mole) can these condensations be effected. Evidently one mole $AlCl_3$ is bound to allylacetate in the form of a complex at the ester group. Subsequently, this complex reacts with benzene at the double bond, but the ether group then undergoes cleavage. In these experiments we obtained 1,2-diphenylpropane in yields of up to 56% of the theoretical. We were also able, by lowering the condensation temperature to 4-6°, to obtain small amounts of β-phenylpropyl acetate which was identified in the form of the corresponding alcohol. In one experiment it was shown that with an excess of benzene, β-phenylpropyl acetate gives 1,2-diphenylpropane. In none of our experiments was allylbenzene obtained.

All these facts justify us in believing that allylacetate actually reacts in the first instance at its double bond. We did not succeed in establishing the conditions in which β-phenylpropyl acetate would be the main product of the condensations. This is due to the ease of cleavage of the ester bond by the excess of $AlCl_3$.

In this group of condensations we thought it was very important to have a strict proof of the structure of the prepared diphenylpropane since the formation of two of its isomers is probable. No proof of this was submitted in previous papers; the authors limited themselves to determination of the constants and to some indirect criteria.

On nitrating 1,2-diphenylpropane, Konovalov [12] obtained a crystalline primary nitro compound which we used for identification of our product, although the reaction proceeds slowly and gives low yields.

By performing the synthesis according to the scheme:



$$C_6H_5CH_2MgCl + C_6H_5COCH_3 \rightarrow C_6H_5CH_2\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle OH}{|}}{C}}-C_6H_5 \rightarrow C_6H_5CH=\overset{\overset{\displaystyle CH_3}{|}}{C}C_6H_5 \rightarrow C_6H_5CH_2\underset{\underset{\displaystyle CH_3}{|}}{CH}-C_6H_5$$

it was possible for us to nitrate two specimens of 1,2-diphenylpropane and to convince ourselves of their identity by the absence of depression of the melting point of a mixture of the two nitro compounds.

EXPERIMENTAL

Examples of condensation of allylacetate with benzene. 1) To 80 ml benzene, mixed with 16.1 g (0.12 mole) $AlCl_3$ was gradually added 10 g (0.1 mole) allylacetate in 20 ml benzene. The mixture was cooled with ice and stirred for 2 hours. After decomposition with acidified water, the benzene layer was separated, dried and fractionated to give 11 g (56%) 1,2-diphenylpropane with b.p. 128-130° at 8 mm; resinous residue 2.5 g.

2) To a solution of 10 g allylacetate in 100 ml benzene at room temperature was gradually added 16.1 g $AlCl_3$. The mixture was heated for $2^1/_2$ hours on a boiling water bath. Yield 11 g (56%) 1,2-diphenylpropane and 3 g resin.

3. To a solution of 15 g (0.15 mole) allylacetate in 150 ml benzene was added 24.2 g (0.18 mole) $AlCl_3$ small portions over a period of $2^1/_2$ hours with continuous cooling and stirring. Stirring was prolonged for another 2 hours. The temperature of the reaction mixture (thermometer in flask) was maintained throughout the whole period at 4-6°. A fraction was collected with b.p. 114-128° at 15 mm (3.4 g); judging by the saponification number, the fraction contained 54% β-phenylpropyl acetate; yield 7% of the theoretical. In addition 11.3 g (38%) 1,2-diphenylpropane was isolated.

Investigation of the products of condensations. β-Phenylpropyl alcohol was isolated by saponification of the 114-128° (15 mm) fraction. Liquid with a pleasant odor. B.p. 113-114° (15 mm).

d_4^{20} 1.0062; n_D^{20} 1.5275; MR_D 41.54; Calculated 41.81.

The p-nitrobenzoate was prepared with m.p. 61-62°. The constants are very close to those reported in the literature [13].

Dehydrogenation of β-phenylpropyl alcohol over copper catalyst at 250-300° and 20-40 mm residual pressure gave hydratropic aldehyde which was isolated via the bisulfite compound. It was identified as the semicarbazone, m.p. 152-153° [14].

1,2-Diphenylpropane. After two distillations the product of the condensations had the following constants: b.p. 128-130° (7 mm); d_4^{20} 0.9818; n_D^{20} 1.5581; MR_D 64.45; Calculated 64.43.

Control synthesis of 1,2-diphenylpropane. Benzylmethylphenyl carbinol [15] was prepared from 40 g benzyl chloride, 7.7 g magnesium and 32 g acetophenone. Yield 37 g (66 %). Dehydration of the carbinol over Al_2O_3 at 400° gave methylstilbene in a yield of 46% of the theoretical. The best results were obtained by boiling the carbinol (22 g) with acetic anhydride (40 g) and acetyl chloride (20 g) [16]. The methylstilbene isolated after neutralization of the solution with soda was recrystallized from alcohol. M. p. 79-80°. Yield 16 g (79.5%).

Methylstilbene (9 g) was reduced to 1,2-diphenylpropane [17] with sodium (9 g) in alcoholic solution (100 ml) by heating the mixture on the boiling water bath. Complete solution of the sodium was effected by addition of 20 ml alcohol, after which the mixture was acidified. The 1,2-diphenylpropane was extracted with ether. Yield 7.7 g (85%).

After distillation over sodium the synthesized product had the following constants: b.p. 128-129° for 7 mm; d_4^{20} 0.9797; n_D^{20} 1.5581; MR_D 64.60.

Nitration of 1,2-diphenylpropane. 5 g diphenylpropane was heated at 100° in a flask, fitted with a mechanical stirrer and a reflux condenser, with 20 ml nitric acid (d 1.075). Heating was continued for 18-20 hours and was stopped after the whole of the hydrocarbon had been transformed into a heavy oil which collected at the bottom of the flask. After separation and washing with soda, the oil was treated with an aqueous alcoholic solution of KOH; only a small portion of the oil went into the alkali solution; from the latter, by passage of CO_2, was gradually separated the nitro compound which crystallized. After washing with aqueous alcohol and recrystallizing from alcohol, the substance had m.p. 153° as reported by Konovalov [12]. Both specimens of 1,2-diphenylpropane gave the same nitro compound, and a mixed sample melted without depression at 153°.

SUMMARY

1. The condensation of allylacetate with benzene in presence of $AlCl_3$ was studied in various conditions. In all cases the main product is 1,2-diphenylpropane (yield up to 56% of the theoretical).

2. At low temperatures (4-6°) the formation was demonstrated of the intermediate β-phenylpropyl acetate, which indicates that the first stage in the condensation is addition at the double bond.

3. Synthesis by a scheme excluding the formation of isomers gave 1,2-diphenylpropane whose nitration by the Konovalov method gave a primary nitro compound which enabled identification of the product of the described condensations.

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*See Consultants Bureau Translation, page 737.

**See Consultants Bureau Translation, page 329.

After 4 minutes [illegible] the [illegible] was [illegible]

Nitration of [illegible] [illegible] was [illegible] a reflux condenser, [illegible] was [illegible] after the whole of the [illegible] of the flask. After [illegible] of [illegible] gradually separated [illegible] from alcohol, the [illegible] gave the same main compound, and a mixed sample [illegible]

1. The condensation of [illegible] in all cases the main product [illegible]

2. At low temperatures [illegible] which indicates that the [illegible]

3. Synthesis by a [illegible] method gave [illegible] compound [illegible]

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THE REACTION OF ETHER-OXIDES WITH NITROGEN COMPOUNDS

VII. REACTION OF GLYCIDE ISOPROPYL AND n-BUTYL ETHERS WITH DIETHYLAMINE

F. G. Ponomarev and V. G. Polosukhina

In previous communications by one of us [1-3] we described the results of experiments on addition of ammonia and diethylamine to methyl and ethyl ethers of glycide. Continuing our investigations, in this paper we describe the results obtained for the interaction of the isopropyl and n-butyl ethers of glycide with diethylamine, data for which are absent from the literature.

The experiments showed that these glycide ethers, like the methyl and ethyl ethers, easily react with aqueous diethylamine, forming the corresponding ethers of aminopropanediol (I) in high yield

$$(C_2H_5)_2NCH_2CHOHCH_2OR \qquad (I)$$

where R = $iso\text{-}C_3H_7$, C_4H_9

This reaction proceeds in one direction and is not accompanied by side reactions, in contrast to the behavior of glycide which polymerizes when diethylamine is added to it during heating [4]: the glycide ethers react smoothly with this amine, independently of the order of mixing of the reactants, at room temperature and at a higher temperature (80-100°).

The structure of the prepared aminoalcohols follows from the method of preparation, in complete accord with the Krasusky rule [5] on the order of addition of ammonia and amines to unsymmetrical *a*-oxides and their substituted derivatives and is confirmed by their synthesis from diethylamine and the corresponding ethers of glycerol *a*-monochlorohydrin

$$ROCH_2CHOHCH_2Cl \xrightarrow{(C_2H_5)_2N} ROCH_2CHOHCH_2N(C_2H_5)_2$$

where R = $iso\text{-}C_3H_7$ and C_4H_9

Esterification of the aminoglycols (I) with acetic anhydride gave the corresponding *a*, *β*-diesters of aminopropanediol (II)

$$(C_2H_5)_2NCH_2CH(OCOCH_3)CH_2OR \qquad (II)$$

The ethers of aminopropanediol (I) are colorless liquids with basic properties, less hygroscopic than the methyl and ethyl ethers of aminopropanediol [2,3]. They react with metallic sodium, rapidly decolorize bromine in chloroform and give crystalline picrates. They do not give crystalline hydrochlorides. When dry hydrogen chloride is passed into absolute ethereal solutions of the aminoalcohols, a viscous noncrystalline mass comes down. Neither do the bases (I) give crystalline derivatives with ethyl iodide.

EXPERIMENTAL

The glycide ethers required for the reaction were obtained from the corresponding ethers of glycerol *a*-monochlorohydrin under the action of pulverized KOH in absolute ether as already described [6]. Diethylamine was used in all the experiments in the form of 33% aqueous solution.

Reaction of glycide isopropyl ether with diethylamine. Synthesis of 3-isopropoxypropanol-2-diethylamine (I, R = $iso\text{-}C_3H_7$).

a) To 17.5 g (0.15 mole) glycide isopropyl ether (b.p. 134°, n_D^{20} 1.4111) was added 33 g (0.45 mole) diethylamine in 58 ml water. The temperature of the mixture was observed to rise from 20 to 30°. When the initially homogeneous reaction mixture was heated on the water bath, it separated into two layers after 10-15 minutes. After heating for 3 hours, the upper layer, which consisted of the aminoalcohol (I), was separated; saturation of the aqueous layer with KOH gave a further small quantity of aminoalcohol which was combined with the main product before drying over KOH and distilling in vacuum. There was obtained 23 g (80%) 3-isopropoxypropanol-2-diethylamine. Here and in all subsequent experiments the yield is calculated on the glycide ether. In two other experiments conducted in precisely the same conditions, the product was obtained in yields of 75 and 77% of the theoretical.

b) To 11.6 g (0.1 mole) glycide isopropyl ether was added 21.9 g diethylamine (0.3 mole) in 44 ml water. The reaction mixture was stood at room temperature for 72 hours. Separation and purification in the above-described manner gave 13.8 g (73%) 3-isopropoxypropanol-2-diethylamine. In another experiment in which the amount of diethylamine was reduced from 3 to 2 moles per mole ether, the yield of product was slightly reduced (64% of the theoretical).

3-Isopropoxypropanol-2-diethylamine had the following constants:

b.p. 93-95° at 10 mm; d_4^{20} 0.9856; n_D^{20} 1.4348; MR_D 55.06; found 55.48.

0.1562 g sub.: 8.3 ml 0.1N H_2SO_4 0.1276 g sub.: 7.00 ml 0.1N H_2SO_4 (Kjeldahl). 0.1154 g sub.: 6 ml 0.1N NaOH. 0.1242 g sub.: 6.7 ml 0.1N NaOH. 0.2456 g sub.: 21.04 g benzene: Δt 0.34°. Found %: N 7.44, 7.46; OH 8.84, 9.17; M 195.8. $C_{10}H_{23}O_2N$. Calculated %: N 7.40; OH 8.98; M 189.29.

Here and in the later experiments the content of hydroxyl group was determined with the aid of acetic anhydride in pyridine [7].

It is a colorless liquid with the odor of imines. It possesses basic properties. It dissolves readily in alcohol, ether, carbon terachloride and benzene, sparingly in cold water and still more sparingly in hot water. It does not distil without decomposition at atmospheric pressure. It is stable when kept for a long period. It reacts with metallic sodium. It rapidly decolorizes a chloroform solution of bromine and potassium permanganate. In normal conditions it absorbs moisture. A quantity of 0.7259 g increased in weight by about 1% after 6 hours.

The picrate, prepared by mixing equimolar alcoholic solutions of the aminoalcohol and picric acid, forms lemon-yellow crystals with m.p. 163-164° (from absolute alcohol).

0.0892 g substance: 8.92 ml 0.1 N H_2SO_4 (Eckert's method [8]). Found %: N 14.00 $C_{16}H_{26}O_9N_4$. Calculated %: N 13.39

The acetate (II. R = iso-C_3H_7) was prepared by the action of acetic anhydride (20% excess) on aminopropanediol. Colorless liquid with a characteristic odor:

B.p. 88° at 8 mm; d_4^{20} 0.9363; n_D^{20} 1.4328; MR_D 64.23; Calculated 64.85.

0.1342 g substance: 5.3 ml 0.1 N H_2SO_4. 0.1210 g substance: 4.9 ml 0.1 N H_2SO_4 (Kjeldahl). Found %: N 5.53; 5.67. $C_{12}H_{25}O_3N$. Calculated %: N 6.05

The acetate is soluble in alcohol and ether; sparingly in water.

Action of diethylamine on the isopropyl ether of glycerol α-monochlorohydrin. With the objective of confirming the structure of the 3-isopropoxypropanol-2-diethylamine prepared from glycide isopropyl ether and diethylamine, we synthesized the same aminoalcohol from the corresponding ether of the haloalcohol and diethylamine. 3 g glycerol α-monochlorohydrin isopropyl ether (b.p. 180-184°, n_D^{20} 1.4405) prepared from epichlorohydrin and absolute alcohol [6], was sealed into a tube with 4.3 g (threefold excess) diethylamine; the mixture was heated on a boiling water bath for 4 hours. The product was then worked up with water; the upper layer was separated; the aqueous layer was saturated with solid KOH to give a small amount of upper layer which was combined with the main product before drying with KOH and distilling in vacuum. Yield 2.7 g (72.6%) aminoalcohol with b.p. 96-98° at 10 mm.

The picrate of this base melted at 163-164° (from absolute alcohol) and did not give a depression with the above-described picrate of the base prepared from glycide isopropyl ether and diethylamine.

0.1264 g substance: 12.41 ml 0.1 N H_2SO_4 (Eckert's method). Found %: N 13.75. $C_{16}H_{26}O_9N_4$. Calculated %: N 13.39.

Reaction of glycide butyl ether with diethylamine. Synthesis of 3-butoxypropanol-2-diethylamine (I. R = C_4H_9)

a) To 23 g (approx. 0.18 mole) glycide butyl ether (b.p. 164-166°; n_D^{20} 1.4178) was added 36.5 g (0.5 mole) diethylamine in 75 ml water. The temperature rose from 20 to 26° and the homogeneous liquid formed two layers after 10-15 minutes. Further procedure was as described above. Vacuum fractionation gave 27 g (76.7%) of 3-butoxypropanol-2-diethylamine. In two other similar experiments this aminoalcohol was obtained in yields of 74 and 77% of the theoretical.

b) To 13 g (0.1 mole) glycide ether was added 22 g (0.3 mole) diethylamine in 44 ml water and the mixture allowed to stand for 72 hours at room temperature. The product was worked up as before to give 13 g (64%) 3-butoxypropanol-2-diethylamine. Using 2 instead of 3 moles of diethylamine per mole glycide ether, the yield fell to 53%.

3-Butoxypropanol-2-diethylamine is a colorless liquid with an imine-like odor.

B.p. 118-119° at 12 mm; d_4^{20} 0.8864; n_D^{20} 1.4340; MR_D 59.71; Calculated 60.11.

0.2304 g substance: 10.9 ml 0.1 N H_2SO_4 (Kjeldahl). 0.1502 g substance: 7.2 ml 0.1 N H_2SO_4. 0.1308 g substance: 6.3 ml 0.1 N NAOH. 0.1164 g substance: 6.1 ml 0.1 N NaOH. 0.1206 g substance: 22.21 g benzene: Δt 0.17°. 0.2330 g substance: 22.21 g benzene: Δt 0.21°. Found %: N 6.62, 6.71; OH 8.21, 8.91; M (mean value) 208.8. $C_{11}H_{25}O_2N$. Calculated %: N 6.89; OH 8.37; M 203.32

It possesses basic properties; dissolves easily in alcohol, ether and benzene; sparingly in cold water and still more sparingly in hot. It is stable after prolonged storage. Distils at atmospheric pressure (180-185°) with much decomposition. Reacts with metallic sodium. Rapidly decolorizes potassium permanganate and bromine in chloroform. In ordinary conditions it takes up moisture. After 6 hours 0.4227 g took up 0.6%.

The picrate forms lemon-yellow crystals with m.p. 166-167° (from absolute alcohol).

0.0642 g substance: 6.3 ml 0.1 N H_2SO_4 (Eckert's method). Found %: N 13.74. $C_{17}H_{28}O_9N_4$. Calculated %: N 12.95.

The acetate (II. $R = C_4H_9$), prepared as described above, is a colorless oil with a characteristic odor.

B.p. 112-113° at 6 mm; d_4^{20} 0.9377; n_D^{20} 1.4344; MR_D 67.99; Calculated 69.47 .

0.1306 g substance: 5.2 ml 0.1 N H_2SO_4. 0.1432 g substance: 5.9 ml 0.1 N H_2SO_4 (Kjeldahl). Found %: N 5.57, 5.77. $C_{13}H_{27}O_3N$. Calculated %: N 5.71.

The acetate is soluble in alcohol and ether, sparingly in water.

Action of diethylamine on glycerol α-monochlorohydrin n-butyl ether. A mixture of 4 g glycerol α-monochlorohydrin n-butyl ether (b.p. 203-205°, n_D^{20} 1.4428) and 5.3 g diethylamine (threefold excess) was heated in a sealed tube on a boiling water bath for 6 hours. The product was then treated with water (9 ml); the top layer was collected, dried with solid KOH and distilled in vacuum. Yield 3.7 g (74.9%) 3-butoxypropanol-2-diethylamine with b.p. 120-121° at 13 mm.

The picrate of this base melted at 166-167° (from absolute alcohol) and did not give a depression with the above-described picrate of the base obtained from glycide butyl ether and diethylamine.

0.1183 g substance: 10.54 ml 0.1 N H_2SO_4. Found %: N 12.44. $C_{17}H_{28}O_9N_4$. Calculated %: N 12.95.

SUMMARY

1. The reaction of glycide isopropyl and n-butyl ethers with aqueous diethylamine was studied.

2. The products of these reactions: 3-isopropoxypropanol-2-diethylamine and 3-butoxypropanol-2-diethylamine and their acetates and some salts were characterized.

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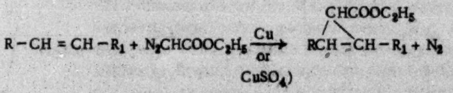
REACTIONS OF ALIPHATIC DIAZO COMPOUNDS WITH UNSATURATED COMPOUNDS

XVII. REACTION OF ETHYLDIAZOACETATE WITH ESTERS OF UNSATURATED ACIDS AND WITH MESITYL OXIDE IN PRESENCE OF COPPER CATALYSTS

I. A. Dyakonov, I. N. Somin and M. I. Komendantov

In previous communications one of us [1] put forward the suggestion that realization of the reaction between ethyldiazoacetate and olefins in presence of copper catalysts



$$R-CH=CH-R_1+N_2CHCOOC_2H_5\xrightarrow[\text{or}\; CuSO_4)]{Cu}\overset{CHCOOC_2H_5}{RCH-CH}-R_1+N_2 \qquad (1)$$

may meet with difficulty when the nucleophilic properties of the ethylenic components in this reaction are weakened by the presence of electron acceptor groups R and R_1 at the double bond. Up to now only one example illustrating this possibility [2] had been known: diethyl fumarate and the diazoacetate do not react with one another with formation of a cyclopropane derivative if the experiment is conducted in presence of copper powder; due to the decomposition of the ethyl diazoacetate on the copper catalyst, only a fresh quantity of ethyl fumarate is obtained [3].

In the present investigation we attempted to increase the number of these examples by studying the heterogeneous catalytic reaction of ethyl diazoacetate with esters of α,β-unsaturated acids—transcrotonic and methacrylic acids—as well as with an α,β-unsaturated ketone—mesityl oxide. It must be pointed out that no data have hitherto appeared in the literature concerning the reaction of carbonyl-containing compounds with aliphatic diazo compounds in presence of copper catalysts. In the absence of catalysts, α,β-unsaturated ketones react with aliphatic diazo compounds in the same manner as do esters of α,β-unsaturated acids [4], i.e., with formation of the corresponding pyrazolines. An example is the reaction of CH_2N_2 with mesityl oxide [5] and of $N_2CHCOOC_2H_5$ with benzalacetophenone [6]. Ketones not containing multiple bonds react with diazomethane usually in the presence of hydroxyl-containing catalysts. Products of the reaction are most usually α-oxides or homologs of the original ketones [7], but in isolated cases the formation occurs of cyclic ketoacetals due to interaction of 2 moles ketones with 1 mole CH_2N_2 [8]. Benzaldehyde reacts similarly with ethyl diazoacetate, in a molar ratio of 2 : 1, in the absence of copper catalyst [9].

In the present communication it is shown that ethyl diazoacetate does not enter into reaction with the ethyl ester of trans-crotonic acid (in presence of copper sulfate) according to equation (1): ($R = CH_3$, $R_1 = COOC_2H_5$). An experiment led to separation of ethyl fumarate—the product of dimerization of $2>CHCOOC_2H_5$ residues—in a yield of 53% of the theoretical. The ester of crotonic acid was recovered to the extent of 60% of the amount calculated from equation (1). In addition a considerable amount of resinous material was obtained.

Reaction did not take place with methylmethacrylate due to fairly rapid polymerization. Taking into account the inhibiting action of copper powder, we may assume that polymerization was accelerated by formation of radicals due to breakdown of the ethyl diazoacetate.

Investigation of the reaction with mesityl oxide showed that the product was an extremely complex mixture of esters, mostly high-boiling, whose separation involved great difficulties. The composition of this complex mixture appears to vary slightly in dependence on the rate of addition of ethyl diazoacetate in the condensation reaction. The slower the addition the closer the elementary composition of the main portion of product to the formula of the ester

$C_{16}H_{26}O_4$. Formation of the latter may be represented by the equation

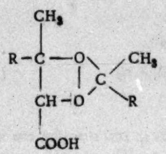
$$N_2CHCOOC_2H_5 + 2(CH_3)_2C{=}CH{-}COCH_3 \xrightarrow[(Cu)]{CuSO_4} C_{16}H_{26}O_4 + N_2. \tag{2}$$

In experiment 1, in which the slowest addition (27 g/hr) was made, fractions 7 and 8 were closest to the composition $C_{16}H_{26}O_4$ (see table) and represented 50.6% by weight of all the fractions. From the lower-boiling portion were isolated fractions 4-5 (6.5% of the total weight), corresponding to the composition $C_{10}H_{16}O_3$:

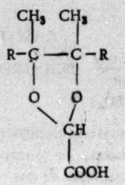
$$N_2CHCOOC_2H_5 + (CH_3)_2C{=}CHCOCH_3 \xrightarrow[(Cu)]{CuSO_4} C_{10}H_{16}O_3 + N_2 \tag{3}$$

and fractions 1-2 (5-6% of the total weight), the main component of which was ethyl glycolate. The remaining fractions enumerated in the table were not examined.

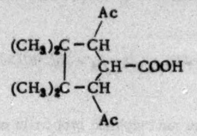
Alkaline hydrolysis of fractions 7-8 gave a small amount of glycolic acid, a mixture of oily acids of indeterminate composition and a solid acid with m.p. 110° with the formula $C_{14}H_{22}O_4$, corresponding to the ester $C_{16}H_{26}O_4$. No explanation has yet been found for the formation of glycolic acid on hydrolysis: its ester could not have come over with the ester $C_{16}H_{26}O_4$ due to the too large difference in boiling points of these compounds. The liquid acids (equivalent 197) were not further investigated. On the basis of the literature data [8, 9] on the formation of cyclic condensation products in reactions of diazo compounds with aldehydes or ketones, we should expect structures (I) or (II) for the acid $C_{14}H_{22}O_4$



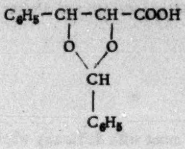
(I)



(II)



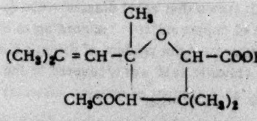
(III)



(IV)

where $R = (CH_3)_2C{=}CH-$ and $Ac = -COCH_3$.

The benzalphenylglyceric acid (IV), obtained by condensation of ethyl diazoacetate with benzaldehyde, hydrolyzes quantitatively to benzaldehyde and phenylgylceric acid [9] on heating with aqueous alcohol or with dilute acetic acid. In these conditions the acid $C_{14}H_{22}O_4$ does not hydrolyze. Under the action of acetic acid, however, it partly changes, possibly into an isomeric acid. Acid $C_{14}H_{22}O_4$ definitely isomerizes in presence of sulfuric acid: on heating together, a small amount of acetone is formed together with an acid of the same composition with m.p. 168° whose structure was not established. None of the anticipated products of hydrolysis were found. The data obtained were not consistent with formulas (I) and (II). Formula (III) could not be taken into consideration in view of the conspicuous unsaturation of acid $C_{14}H_{22}O_4$ (see below). We decided on the structure of the tetrahydrofuran carboxylic acid (V)*, although we failed in the course of further investigation to obtain conclusive evidence in support of this conclusion.



(V)

Starting from this formula, we may assume that 2% H_2SO_4 causes ring expansion with participation of the carbonyl of the acetyl group: the product of isomerization does not give a precipitate with 2,4-dinitrophenylhydrazine in contrast to the original acid. Acetone is evidently formed due to a side reaction of hydration of the isobutenyl group similar to that observed for mesityl oxide in the same conditions [10].

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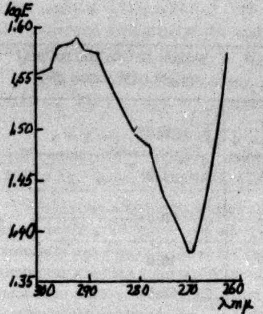
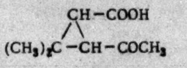
* Here we give only one of the four possible (for the given reaction) formulas of trimethyl-isobutenylacetyl-tetrahydrofuran carboxylic acid.

The acid with m.p. 110° does not hydrogenate over Raney Ni in alcoholic solution at the ordinary temperature. In the same conditions it slowly adds on hydrogen in presence of platinum. The consumption of hydrogen exceeds that calculated for one double bond (40% excess). If formula (V) is correct, then the excess must be due to hydrogenolysis of the ether bond of the ring: in the hydrogenation product the active hydrogen content was higher than that calculated for $C_{14}H_{24}O_4$. The reaction with 2,4-dinitrophenylhydrazine gave a positive result. Rupture of the ring of the investigated acid evidently also accounts for the increased permanganate consumption during oxidation over that calculated for one double bond (70% excess). In the products of this reaction were found acetone and a little acetic acid (possibly due to further oxidation of the acetone), but instead of the expected dibasic acid $C_{11}H_{16}O_5$ more drastic oxidation gave a mixture of non-crystallizing acids whose analysis did not give definite results. Evidently the screening action of substituents on the ring hinders the formation of derivatives at the carbonyl group of the acid. A precipitate is only formed with 2,4-dinitrophenylhydrazine. The presence of a carbonyl group was conclusively demonstrated only by the ultraviolet spectrum of the acid. The acid has a maximum of absorption at $\lambda = 292$ mμ, i.e., in the region of adsorption of the C = O group. Fractions 4-5 were a mixture of isomeric esters $C_{10}H_{16}O_3$. Their alkaline hydrolysis gave (yield 15% of the theoretical) trans-3,3-dimethyl-2-acetylcyclopropane-1-carboxylic acid (VI), and formation of acetone was detected.

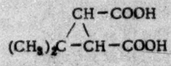


Absorption curve of acid $C_{14}H_{22}O_4$ Solvent 95% alcohol. Concentration: 0.02 mole/liter. Beckmann SF-11 spectrophotometer.

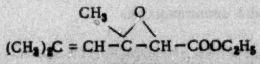
Oxidation of acid (VI) with sodium hypobromite gave trans-caronic acid (VII). Formation of acetone on hydrolysis and some qualitative reactions of the investigated fractions make probable the presence of the isomeric esters (VIII) and (IX) in the mixture. The presence of small amounts of water in the condensation product readily brings about hydrolysis of (IX) with formation of mesityl oxide and the ester of glycolic acid, which, as already mentioned, was found in Fractions 1-2. Judging by the analytical data for Fractions 4-5 (about 2% active hydrogen found) the presence in the mixture of a hydroxyl-containing ester (structure not established) can also be assumed. The presence of only trimethylene carboxylic ester can be said to be conclusively established in these fractions.



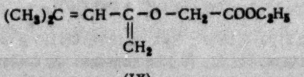
(VI)



(VII)

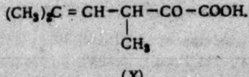


(VIII)



$$(CH_3)_2C=CH-\underset{\underset{CH_2}{\|}}{C}-O-CH_2-COOC_2H_5$$

(IX)



$$(CH_3)_2C=CH-\underset{\underset{CH_3}{|}}{CH}-CO-COOH.$$

(X)

If addition of ethyl diazoacetate to mesityl oxide is effected more slowly than in experiment I (see experiment III), the main portion of the condensation product (54.9% of the weight of all the fractions) rather sharply deviates in composition from that calculated for $C_{16}H_{26}O_4$. Alkaline hydrolysis of this portion gives, apart from the acids obtained on hydrolysis of fractions 7-8 of experiment I, an unsaturated keto acid of the composition $C_8H_{12}O_3$ for which formula (X) may be advanced. The ethyl ester of this acid must have the composition $C_{10}H_{16}O_3$, and possibly its presence in the condensation brought about the above-noted change of composition.

Although our investigation is not complete, we can nevertheless draw a conclusion of interest to us concerning the behavior of the double bond in this reaction. It may be concluded, taking into account the insignificant yield of cyclopropane ether, that not the double carbon-carbon bond but the nucleophilic oxygen atom of mesityl oxide is the point of attack of the reagent – the $>CHCOOC_2H_5$ radical – in this reaction. In all probability, one of the esters – (VIII) or (IX) – is the primary product of interaction, while ester $C_{16}H_{26}O_4$ is formed by secondary reaction of mesityl oxide with one of these compounds

However that may be, mesityl oxide or the esters of α,β-unsaturated acids concerned here cannot serve as a starting point for the preparation of derivatives of cyclopropane in this reaction. This result, in our opinion, may be explained by a certain similarity of the electronic characteristics of the double bonds in the starting olefins.

EXPERIMENTAL

1. Reaction of Ethyl Diazoacetate with Mesityl Oxide

Experiment I. Starting Components. Ethyl diazoacetate was purified by steam distillation in vacuum [11]. Mesityl oxide was rectified in a column; b.p. 126-130° [12]. The catalyst was anhydrous copper sulfate.

Condensation. To mesityl oxide (1230 g) and 4 g copper sulfate, heated to boiling on an oil bath, was slowly added dropwise with mechanical stirring a mixture of 400 g ethyldiazoacetate and 360 g mesityl oxide. The mean rate of addition was 27 g ethyl diazoacetate per hour. Bath temperature 130-140°. After nitrogen had ceased to come off (at the end of the experiment 93.4% of the calculated amount had come off) the reaction product was cooled and filtered and the excess mesityl oxide distilled off in vacuum: b.p. 60-70° at 60-65 mm, yield 1230 g. The residue was an oily liquid which was vacuum-distilled. The distillate weighed 530 g and boiled at 61° at 7 mm to 145° at 0.5 mm. Only the small low-boiling portion of the distillate was further fractionated in a vacuum column at 7 mm to 1 mm. The main high-boiling portion was distilled in a vacuum of less than 1 mm from a Wurtz flask with a low and broad side tube. The fractions resulting from repeated fractionation are set forth in the table.

Results of Fractional Distillation in Vacuum of the Condensation Product

No. of fraction	B.p. (°C)	Index of refraction n_D^{20}	Weight (g)	Weight in relation to total weight of fraction (%)
1	47.5-61 at 5 mm	1.4205	5.5	5.4*
2	51-55 at 5 mm	1.4188	17.0	
3	55-92	From 1.4206 to 1.4430	4.3	1.0
4	60-63 at 1 mm	1.4482	22.0	6.5*
5	60-63 at 1 mm	1.4510	5.0	
6	68-105 at 0.5 mm	From 1.4555 to 1.4654	62.1	15.0
7	105-115 at 0.5 mm	1.4701	95.0	50.6*
8	105-115 at 0.5 mm	1.4711	115.0	
9	105-130 at 0.5 mm	From 1.4730 to 1.4780	50.7	12.2
10	130-145 at 0.5 mm (with decomposition)	From 1.4780 to 1.4838	38.4	9.3

Investigation of first and second fractions. Both fractions, especially the first, contain, together with the ester of glycolic acid, mesityl oxide (characteristic odor, decolorization of $KMnO_4$, 2,4-dinitrophenylhydrazine test); this contamination also resulted (for the second fraction) in the not fully satisfactory analytical data and constants: b.p. 51-55° at 5 mm; d_4^{20} 1.0921; n_D^{20} 1.4188 (literature data: b.p. 158° at 760 mm; d_4^{15} 1.087 [10]).

0.1598, 0.1979 g substance: 0.2754; 0.3435 g CO_2; 0.1130, 0.1343 g H_2O. 0.1074, 0.1197 g substance: 24.1, 26.7 ml CH_4 (14°, 773.9 mm). 0.1037, 0.2035 g substance: 11.31, 18.13 g benzene: Δt 0.40; 0.50°. Found %: C 47.02, 47.37; H 7.91, 7.59; OH 16.32, 16.43; M 117.6, 115.2. $C_4H_8O_3$. Calculated %: C 46.15; H 7.74 OH 16.34; M 104.1.

Fraction 1 was not analyzed. Hydrolysis of 13.3 g of the second fraction with 100 ml 2 N NaOH followed by ether extraction of the acidified solution in a perforator gave 2.25 g glycolic acid with m.p. 78-79° (pressed on a plate and recrystallized from ether). It was identified by the mixed melting point test and by a determination of the equivalent.

0.1666 g substance: 21.83 ml 0.1 N NaOH. Found: equiv. 76.31. $(CH_2O)COOH$. Calculated: equiv. 76.06.

Hydrolysis of fraction 1 by heating with 10% HCl followed by evaporation of the solution likewise led to formation of glycolic acid.

Examination of fractions 4 and 5. Both fractions decolorized 2% $KMnO_4$, gave the silver mirror reaction with ammoniacal Ag_2O, and in the cold deposited iodine from a solution of KI in acetic acid.

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*Calculated for sum of weights of both fractions.

Fraction 4: b.p. 60-64° at 1 mm; d_4^{20} 1.002; n_4^{20} 1.4482

0.1274, 0.1616 g substance: 0.3065, 0.3851 g CO_2; 0.1019, 0.1277 g H_2O. 0.1459 g substance: 4.1 ml CH_4 (13.5°, 768.4 mm) 0.2214 g substance: 14.72 g benzene: Δt 0.44°. Found %: C 65.61, 65.04; H 8.74 8.84; OH 2.0; M 175. $C_{10}H_{15}(OH)$. Calculated %: C 65.19; H 8.76; OH 9.8; M 184.2

Fraction 5: b.p. 64-68° at 1 mm; d_4^{20} 1.004; n_D^{20} 1.4510.

0.1141 g substance: 0.2726 g CO_2; 0.0903 g H_2O. 0.1416 g substance: 12.86 g benzene: Δt 0.29°. 0.4184 g substance: 11.5 ml 0.2 N KOH (hydrolysis). 0.1875 g substance: 5.0 ml CH_4 (13.5°, 768.4 mm). Found %: C 65.18; H 8.85; $M_{cr.}$ 168.0; $M_{hyd.}$ 182.0; OH 1.9. $C_{10}H_{15}OH$. Calculated %: C 65.19; H 8.76; M 184.2; OH 9.8.

Trans-3,3-dimethyl-2-acetylcyclopropane-1-carboxylic acid (VI). 5.4 g (0.3 mole) fraction 4 was hydrolyzed by heating for an hour with 25 ml 10% NaOH. The solution was steam-distilled. When the first portion of the distillate was mixed with an acetic acid solution of 4-nitrophenylhydrazine, it gave a yellow precipitate with m.p. 141-143° (0.2 g); after crystallization from aqueous alcohol the m.p. was 145-146°; identity was confirmed by a mixed melting point test with acetone 4-nitrophenylhydrazone.

The alkaline solution was acidified and the resultant oily acid was extracted with ether. The crystals obtained after removing the ether and drying in vacuum were pressed on a porous plate and crystallized from a mixture of ether and ligroine. M.p. 108-110°. Yield of acid (VI) 0.66 g (14%). Heating of fraction 5 for 3 hours with 10% NaOH led to formation of 0.71 g acid (VI) (15% of the theoretical yield) and 0.6 g acetone 4-nitrophenylhydrazone. In both cases prolonged extraction of the acid solution gave an insignificant amount of oily material which was not amenable to examination.

Acid (VI) is soluble in alcohol and ether, sparingly in water. It does not decolorize in the cold a solution of $KMnO_4$. Its silver salt was prepared.

0.1116 g sub.: 0.2525 g CO_2; 0.0797 g H_2O. 0.1002 g sub.: 6.4 ml 0.1N NaOH. Found %: C 61.76; H 7.97; equiv. 156.3. $C_8H_{12}O_3$. Calculated %: C 61.52; H 7.75; equiv. 156.2. 0.1566, 0.1367 g sub.: 0.0640, 0.0560 g Ag. Found %: Ag 40.87, 40.96. $C_8H_{11}O_3Ag$. Calculated %: Ag 41.00.

Oxidation with hypobromite: trans-carboxylic acid (VII). A solution of 0.75 g acid (VII) in 2.4 ml 10% NaOH was run in the cold into a cold solution of sodium hypobromite (44 ml H_2O, 2.64 g NaOH and 3.5 g bromine); bromoform was evolved. After the lapse of 2 hours, the solution was saturated with SO_2 and made alkaline; the bromoform was then extracted with ether. The aqueous layer was acidified with sulfuric acid and saturated with ammonium sulfate; this brought down a solid carboxylic acid which was extracted with ether. After careful evaporation of the solvent in the cold, the acid (VII) was twice recrystallized from hot water. M.p. 211° in agreement with the literature [10]. Yield 0.60-0.64 g or 80-85% of the theoretical. The acid equivalent and the silver content of the prepared salt were determined.

0.1511 g sub.: 19.0 ml 0.1N NaOH. Found: equiv. 79.49. $C_5H_8(COOH)_2$. Calculated: equiv. 79.08. 0.1983, 0.1509 g sub.: 0.1136, 0.0864 g Ag. Found %: Ag 57.28, 57.37.. $C_7H_8O_4Ag_2$. Calculated %: Ag 58.01.

Examination of fractions 7 and 8. Fraction 7, b.p. 105-115° at 0.5 mm; n_D^{20} 1.4701.

0.1471 g sub.: 0.3628 g CO_2; 0.1220 g H_2O. 0.2497 g sub.: 21.39 g benzene: Δt 0.20°. Found %: C 67.32; H 9.28; M 268.9. $C_{16}H_{26}O_4$. Calculated %: C 68.05; H 9.28; M 282.4.

Fraction 8: b.p. 105-115° at 0.5 mm; n_D^{20} 1.4711.

0.1280 g sub.: 0.3174 g CO_2; 0.1035 g H_2O. 0.1692 g sub.; 18.99 g benzene: Δt 0.17°. Found %: C 67.69; H 9.05; M 299.0. $C_{16}H_{26}O_4$. Calculated %: C 68.05; H 9.28; M 282.4.

Alkaline hydrolysis of fraction 7. 80 g of the substance was hydrolyzed by heating with 350 ml 10% KOH. Dark-red solution. After concentration on the water bath it was acidified with 30% sulfuric acid which was introduced in 10 ml portions beneath a layer of ether which had been poured on to the surface of the cooled alkaline solution. The organic acid which separated as an oil after acidification went into the ether layer which was periodically poured off and replaced by fresh ether. From the ethereal extracts was obtained 59 g oily acid which was distilled in vacuum (0.5 mm) from a Wurtz flask with a broad side tube. The first fraction of distillate crystallized in the side tube. The distillation was stopped and the crystals pressed on porous plate. M.p. 76-79°. Yield of crude glycolic acid 2 g. M.p. (from ether) 79-80°.

20.00 mg sub.: 23.14 mg CO_2; 9.60 mg H_2O. 0.1613 g sub.: 23.71 ml 0.1N NaOH. Found %: C 31.57; H 5.37; equiv. 75.61. $(CH_2O)COOH$. Calculated %: C 31.59; H 5.34; equiv. 76.05.

Distillation was resumed and a distillate obtained in the form of a very viscous oil with b.p. 115-135° (0.5 mm). It was separated into four fractions, differing from one another by viscosity and color: the viscosity increases in the later fractions, which have the appearance of vaseline; the color deepens from yellow in the first fraction to red-brown in the last. The two top fractions slowly crystallized when rubbed with a rod. On seeding, the lower fractions also crystallized but to a lesser degree. After standing for 48-72 hours all the fractions were filtered under vacuum through a porous Schott filter and the obtained crystals, as well as the filtrates, were combined. The crystals were washed with absolute ether and pressed on porous plate. Yield of crude acid $C_{14}H_{22}O_4$ with m.p. 100-104° was 10 g (14%). Crystallization from a mixture of ether and ligroine gave 6 g nearly colorless crystals with m.p. 108°. The pure preparation melted at 109-110°.

The oily filtrate, separated from the solid acid $C_{14}H_{22}O_4$ was again distilled in vacuum to give a yellow distillate (fairly viscous) and a small quantity of glycolic acid. The equivalent of the distillate was determined:

1.0150 g sub.: 51.18 mg 0.1N NaOH. Found: equiv. 197.6.

The distillate was not further examined. Glycolic acid was also isolated by prolonged ethereal extraction in a perforater of the acidic aqueous solution remaining after separation of the investigated mixture of acids.

Alkaline hydrolysis of fraction 8 (97 g substance, 430 ml 10% KOH) also led to formation of glycolic acid and acid $C_{14}H_{22}O_4$. 14 g of the latter (16%) was obtained; m.p. 102-105°. Crystallization gave 9 g with m.p. 107-108°.

Examination of acid $C_{14}H_{22}O_4$. M.p. 109-110°. Readily soluble in alcohol, less soluble in ether, insoluble in water. Decolorizes cold $KMnO_4$ solution.

0.1180, 0.1306 g sub.: 0.2865, 0.3185 g CO_2; 0.0942, 0.1038 g H_2O. 0.2250, 0.1548 g sub.: 8.85, 6.96 ml 0.1N NaOH. 0.0948 g sub.: 9.10 ml CH_4 (15°, 754.4 mm). Found %: C 66.27, 66.58; H 8.93, 8.92; act. H 0.404; equiv. 254.4, 255.7. $C_{14}H_{22}O_4$. Calculated %: C 66.12; H 8.72; act. H 0.396; equiv. 254.3.

Hydrogenation. The acid does not undergo hydrogenation over Raney nickel in alcoholic solution at room temperature. Hydrogenation of 1 g acid in alcohol (50 ml) in presence of 0.2 g Pt at 16° and 765 mm lasted 11 hours at an initial hydrogen absorption velocity of 15 ml in 30 minutes and a total H_2 consumption of 130 ml (0°, 760 mm), which exceeds by 45% the amount of hydrogen calculated for one double bond. The product of hydrogenation is a noncrystallizing, colorless oil, fairly viscous. The number of active hydrogens was found to be higher than calculated for $C_{14}H_{24}O_4$.

0.1091 g sub.: 12.0 mg CH_4 (15°, 754 mm). Found: act. H 0.458. Calculated: act. H 0.393.

Reaction with reagents at the carbonyl group. The semicarbazone and p-nitrophenylhydrazone of the acid could not be prepared by the usual procedures. On interaction of 1 g of 2,4-dinitrophenylhydrazine in a solution of 25 ml alcohol, 7.5 ml water and 5 ml conc. sulfuric acid [14] with an alcoholic solution of 0.5 g of the acid, a precipitate of hydrazone was only obtained after several hours. M.p. 102-105°. After three crystallizations from alcohol the m.p. was constant at 180-181°. Owing to lack of material it was not analyzed. See diagram for ultraviolet absorption spectrum of the acid.

Action of aqueous alcohol. The original acid was recovered unchanged after 45 minutes boiling of a solution of the acid in 50% alcohol followed by removal of the solvent on the water bath.

Action of 20% acetic acid. 0.5 g acid in solution in 20% acetic acid (20 ml) was refluxed for an hour. Removal of the solvent left 0.4 g yellowish, viscous mass, acidic in character. Analysis of the silver salt showed that hydrolysis had not taken place since the silver content of the salt did not differ from that calculated for the salt of the original acid (or its isomer).

0.1659 g sub.: 0.0491 g Ag. Found %: Ag 29.59. $C_{14}H_{21}O_4Ag$. Calculated %: Ag 29.86.

Action of 2% sulfuric acid. 0.5 g acid and a solution of 2% H_2SO_4 with a small addition of alcohol (for dissolving the acid) were heated for 2 hours under a reflux condenser and the solution was then steam-distilled. A little acetone was detected in the distillate with the help of the p-nitrophenylhydrazine test. Ether extraction in a perforator of the remaining aqueous solution yielded resin-containing crystals which were recrystallized from aqueous alcohol. M.p. 167-168°, colorless crystals. Yield 0.2 g or 40% of the weight of the original acid. A second experiment was performed with 3 g acid and acetone was detected in the form of the 2,4-dinitrophenylhydrazone; yield of acid with m.p. 167-168° 1.4 g or 46% of the original weight. The analytical data for the acid and its silver salt are consistent with the formula $C_{14}H_{22}O_4$.

10.15 mg sub.: 24.84 mg CO_2; 7.78 mg H_2O. 0.2058 g sub.: 8.05 ml 0.1N NaOH. Found %: C 66.79; H 8.58; equiv. 255.8. $C_{14}H_{22}O_4$. Calculated %: C 66.12; H 8.72; equiv. 254.3. 0.0907 g sub.: 0.0270 g Ag. Found %: Ag 29.77. $C_{14}H_{21}O_4Ag$. Calculated %: Ag 29.86.

The acid is readily soluble in alcohol but less soluble than the original acid in ether and insoluble in water. A solid 2,4-dinitrophenylhydrazone is not formed even after prolonged standing of the acid with the reagent.

Oxidation of the acid $C_{14}H_{22}O_4$ with m.p. 109-110°. 5 g of the acid was oxidized in alkaline solution with 2% $KMnO_4$ solution (in the cold). Consumption of oxidizing agent was 10.5 g (170% of that calculated for one double bond). After working up in the usual manner, acetone was isolated from the neutral reaction products (as the p-nitrophenylhydrazone), while ether extraction of the acid products gave a small amount of acetic acid and 3.6 g of a glutinous, noncrystallizing acid with a dark-red color. Both acids were converted into their silver salts and the neutralization equivalent of the second acid was determined.

0.2345 g sub.: 0.1510 g Ag. Found %: Ag 64.40. $C_2H_3O_2Ag$. Calculated %: Ag 64.63. 0.2239, 0.2336 g sub.: 0.2465, 0.2573 g CO_2; 0.0722, 0.0766 g H_2O; 0.0970, 0.1010 g Ag. Found %: C 30.04, 30.05; H 3.61, 3.67; Ag 43.35, 43.23. $C_{11}H_{14}O_6Ag_2$. Calculated %: C 28.84; H 3.08; Ag 47.11. 0.2770 g sub.: 18.82 ml 0.1N NaOH. Found: equiv. 147.2. $C_{11}H_{16}O_6$. Calculated: equiv. 122.1.

Judging by the analytical data, the noncrystallizing acid is not pure but a mixture of acids. Attempts to separate them by fractional precipitation of the silver salts were unsuccessful. The phenacyl ester was a liquid.

2. Reaction of Ethyl Diazoacetate with Mesityl Oxide in Experiments II and III

Experiments II and III were carried out by the same procedure as Experiment I, except for a change in the mean rate of addition of $N_2CHCOOC_2H_5$ to mesityl oxide (expt. II – 35 g/hr.: expt. III – 40 g/hr.) and a different molar ratio reagents (1:4 in experiments II and III against 1:4.6 in expt. I). Below are set forth the analytical data characterizing the principal fractions obtained on fractional distillation of the crude product of these experiments (compare the data for fractions 7 and 8 of expt. I, distilling in approximately the same temperature range).

Expt. II. Fraction with $n_D^{17.5}$ 1.4692–1.4730 (53% of the weight of all the fractions).

0.0992, 0.1529 g sub.: 0.2431, 0.3729 g CO_2; 0.0817, 0.1269 g H_2O. 0.1726, 0.1718 g sub.; 15.50, 15.65 g benzene: Δt 0.19, 0.19°. Found %: C 66.73, 66.56; H 9.22, 9.26; M 300.6, 296.3. $C_{16}H_{26}O_4$. Calculated %: C 68.06; H 9.28; M 282.3.

Expt. III. Fraction with n_D^{20} 1.466; d_4^{20} 1.040 (54.9% of weight of all fractions).

0.1204, 0.1267 g sub.: 0.2873, 0.3018 g CO_2; 0.0944, 0.0985 g H_2O. 0.3212, 0.3565 g sub.; 12.97, 14.21 g benzene: Δt 0.45, 0.47°. Found %: C 65.13, 65.00; H 8.77, 8.70; M 282.3, 273.8. $C_{16}H_{26}O_4$. Calculated %: C 68.06; H 9.28; M 282.3.

80 g of this fraction was subjected to hydrolysis with 10% KOH in the conditions described in expt. I. From the products of this reaction, apart from a mixture of oily acids, were isolated glycolic acid (0.7 g) and, in contrast to expt. I, a solid acid with m.p. 63° (from ether-ligroine) in a weight of 7.0 g. Repeated crystallizations from the same solvent gave m.p. 64-65°.

0.1267, 0.1083 g sub.: 0.2990, 0.2658 g CO_2; 0.0955, 0.0820 g H_2O. 0.1339 g sub.: 6.79 ml 0.1N NaOH. 0.1054 g sub.: 11.25ml CH_4 (11.5°, 759 mm). Found %: C 64.40, 64.71; H 8.43, 8.47; equiv. 197.2; OH 7.86. $C_{14}H_{22}O_4$. Calculated %: C 66.11; H 8.72; equiv. 254.3; OH 6.68. $C_8H_{12}O_3$. Calculated %: C 61.51; H 7.74; equiv. 156.2; OH 10.88.

The data suggest the formation of a mixture of acids which cannot be separated by crystallization from ether. Fractionation was found possible by treatment of the mixture (6.7 g) with a large amount of hot water: the water-insoluble portion (2.5 g) had m.p. 106-108° (from aqueous alcohol) and was identified by the mixed test with acid $C_{14}H_{22}O_4$ (m.p. 109-110°). From the solution was isolated (by ether extraction) another acid with m.p. 71-72°, 0.9 g; after crystallization from ether-ligroine the m.p. was 72-73°.

0.1262, 0.1249 g sub.: 0.2853, 0.2835 g CO_2; 0.0871, 0.0886 g H_2O. 0.1072 g sub.: 16 ml CH_4 (12.5°, 751.5 mm). 0.1167 g sub.: 7.44 ml 0.1N NaOH. Found %: C 61.79, 61.94; H 7.72, 7.94; OH 10.82, equiv. 156.8. $C_8H_{12}O_3$. Calculated %: C 61.51; H 7.74; OH 10.88, equiv. 156.2.

The acid is poorly soluble in cold water, easily in alcohol, less easily in ether; it decolorizes permanganate solution in the cold; with an acetic acid solution of p-nitrophenylhydrazine it gives a yellow solid with m.p. 135-137°.

In addition expt. III gave fractions with approximately the same constants as in expt. I: b.p. 68-75° at 2 mm, $n_D^{19.2}$ 1.4490-1.4530. They comprised 10% of the whole weight. The middle one of these fractions with b.p. 71.5-73° at 2 mm; $n_D^{19.2}$ 1.4520 (6.5% of the weight of the whole distillate) was analyzed.

0.1141 g sub.: 0.2726 g CO_2; 0.0903 g H_2O. 0.2547 g sub.: 13.07 g benzene: Δt 0.603°. 0.4184 g sub.: 11.5 ml 0.2 N KOH (hydrolysis). Found %: C 65.18; H 8.85; $M_{cr.}$ 165.8; $M_{hyd.}$ 182.0. $C_{10}H_{16}O_3$. Calculated %: C 65.19; H 8.76; M 184.2.

Qualitative reactions were the same as for fractions 4 and 5 in expt. I. A fraction corresponding to glycolic ester was not isolated.

3. Reaction of Ethyl Diazoacetate with the Ethyl Ester of Trans-Crotonic Acid

0.5 g copper sulfate, 80 g (0.07 mole) ethyl crotonate with b.p. 136-138° and 40 g (0.35 mole) pure ethyl diazoacetate were reacted as described previously. At the end of the reaction 63.6 g crotonic ester (5.57 moles) was regenerated as compared with the calculated amount (0.35 mole); b.p. 35-37° at 14 mm. The residual reaction product (39 g) was distilled in a 10 mm vacuum: b.p. 95-105°, $n_D^{16.1}$ 1.4410. Yield of crude fumaric ester: 16.2 g (53%). Literature data [13]: b.p. 218.4°; n_D^{20} 1.4410; d_4^{15} 1.057. About 20 g of undistillable resins were obtained. After redistillation in vacuum the ester was characterized by its constants and by analysis:

d_4^{20} 1.055; n_D^{20} 1.440.

0.1505 g sub.: 0.3069 g CO_2; 0.1005 g H_2O. Found %: C 55.54; H 7.46. $C_8H_{12}O_4$. Calculated %: C 55.58; H 7.03. $C_{10}H_{16}O_4$. Calculated %: C 63.10; H 8.47.

In addition diphenacyl fumarate was obtained with m.p. 196-197° (from alcohol), and was identified by comparison with an authentic sample.

4. Reaction of Ethyl Diazoacetate with Methyl Methacrylate

Dropwise addition was made slowly with stirring to 120 g methyl methacrylate (b.p. 100-101°) at the boil (with 0.5 g copper powder) of a solution of 31 g ethyl diazoacetate in a volume equal to that of the methacrylate. Nitrogen was given off. After an hour polymerization had proceeded to a degree such that the reaction product did not flow out of the flask.

A blank experiment (without ethyl diazoacetate) run in the same conditions showed much less polymerization after one hour.

SUMMARY

1. Interaction of ethyl diazoacetate with esters of trans-crotonic and methacrylic acid in presence of copper or copper sulfate does not lead to formation of the corresponding esters of cyclopropane carboxylic acids. In the former case the product of reaction is fumaric ester; in the second case rapid polymerization sets in before the completion of the experiment.

2. Interaction of ethyl diazoacetate with mesityl oxide in presence of copper catalysts proceeds in various directions and leads to formation of an extremely complex mixture of esters. The main direction of this interaction when there is a large excess of mesityl oxide in the reaction is condensation of two molecules of mesityl oxide with one molecule of ethyl diazoacetate. Secondary reactions are condensation of reactants in 1:1 molar ratio and formation of ethyl glycolate.

3. The ester of 3,3-dimethyl-2-acetylcyclopropane carboxylic acid was found only to an insignificant extent among the various substances formed in this condensation and investigated in this communication.

4. The results obtained in this communication have been shown to fit in with previously formulated [1, 2] theoretical considerations about the laws regulating the interaction of ethyl diazoacetate with olefins in presence of copper catalysts.

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BORON FLUORIDE AS A CATALYST IN ORGANIC CHEMISTRY

IX. ALKYLATION OF o- AND p-CHLOROPHENOLS WITH 2-PENTENE IN PRESENCE OF BORON FLUORIDE ETHERATE

S. V. Zavgorodny and E. M. Faustova

Alkyl phenols and alkyl phenol ethers are widely used at the present time as antioxidants, as starting materials for synthesis of high-quality oil-soluble resins, pharmaceuticals, etc.. Alkyl halophenols and alkyl ethers of halophenols possess germicidal and insecticidal properties and are therefore of definite interest.

The simplest, most convenient and most accessible method of their preparation is the alkylation of phenols and halophenols with olefins in presence of various catalysts.

We have studied the alkylation of o- and p-chlorophenols with 2-pentene, obtained as a by-product in the production of synthetic rubber by the Lebedev process, in presence of boron fluoride etherate as catalyst.

Alkylation was studied at a temperature of 16-18° on a boiling water bath using various ratios of reactants in presence of 5-7% of catalyst.

It was established that o- and p-chlorophenols are alkylated by 2-pentene in presence of boron fluoride etherate with formation of a mixture of ethereal and phenolic products. The quantitative ratio between the ethereal and phenolic compounds depends on the temperature, the duration of reaction and the ratios of the main components. As a rule, rise of temperature from room to 100° promotes speedier reaction. For instance, on interaction of o-chlorophenol with 2-pentene in molar ratios, nearly identical yields of ethereal compounds (36%) are obtained at room temperature in the course of 5 days and at 100° in the course of 4 hours. At 100° the duration of reaction has the effect that up to 4 hours the yield of ethereal compounds rises, while subsequently, up to 16 hours it decreases slightly. At the same time the yield of phenolic compounds increases. These observations once again confirm the correctness of the hypothesis that alkylation of phenols with olefins at higher temperatures proceeds through formation of alkyl ethers and isomerization of these to alkyl phenols. However, this hypothesis does not exclude the possibility also of direct alkylation of the benzene ring of phenolic ethers, especially at relatively low temperatures.

EXPERIMENTAL

Starting materials. The chlorophenols needed for reaction were used in the form of ordinary commercial preparations. o-Chlorophenol, freshly distilled with b.p. 171-173° and d_{20}^{20} 1.2480. p-Chlorophenol without previous recrystallization. 2-Pentene was isolated from the still residues of production of synthetic rubber by the S. V. Lebedev process [1].

Alkylation procedure. Chlorophenols and $BF_3 \cdot O(C_2H_5)_2$ were introduced into a small flask. The mixture was cooled with snow and 2-pentene was added. The homogeneous, readily mobile, light-brown liquid was left at room temperature for a definite period in the closed flask or heated on the boiling water bath. It was then treated with 5% aqueous NaOH until the phenolic products had completely separated, i.e. until a drop of the alkali-insoluble mass gave a turbidity with dilute hydrochloric acid. Thereupon the ethereal compounds (in the form of a pleasant-smelling oily liquid) were separated from the aqueous-alkaline solution of phenolic compounds, washed with water, dried with ignited sodium sulfate or potassium carbonate and distilled. Fractions were collected over a wide temperature interval. A small quantity of viscous, black resin, readily soluble in ether, always remained in the distillation flask.

The alkaline solutions of phenolic products were treated with dilute hydrochloric acid until neutral. The regenerated phenols were separated, washed with water, dried and distilled (like the ethereal compounds) over a wide temperature interval.

The experimental data for the reaction with o-chlorophenol are set forth in Table 1, and those for p-chlorophenol in Table 2.

TABLE 1

Alkylation of o-Chlorophenol with 2-Pentene in Presence of $BF_3 \cdot O(C_2H_5)_2$

No. of expt.	Taken for reaction				Molar ratios of phenol to 2-pentene	Conditions of reaction		Products obtained					
	o-Chlorophenol (in g)	2-Pentene (in g)	$BF_3 \cdot O(C_2H_5)_2$			Temp.	Duration (in hrs)	Ethereal type			Phenolic type		
			(in g)	(in %)				in g	in %*	b.p.	in g	in %*	b.p.
1	12.73	6.44	1.06	6.2	1:1	Room	5 days	6.26	34.30	50-125° (10 mm)	1.42	7.78	180-250°
2	10.36	5.70	1.25	7.8	1:1	95-97°	2	4.54	28.32	210-296	3.71	23.14	200-267
3	13.27	6.55	0.95	4.8	1:1	95-97	4	6.53	35.18	125-240 (10 mm)	2.33	12.55	180-255
4	12.18	7.70	1.24	6.2	1:1	95-97	16	5.48	27.56	120-210 (10 mm)	4.13	20.77	180-260
5	6.43	6.40	1.10	8.6	1:2	95-97	4	5.33	41.54	120-168 (13 mm)	3.20	24.94	180-260
6	13.70	3.65	1.25	7.2	2:1	95-97	4	2.95	28.53		6.15	59.48	180-260

We see from Table 1 that o-chlorophenol is alkylated by 2-pentene in presence of 6% $BF_3 \cdot O(C_2H_5)_2$ at room temperature with formation of almost exclusively ethereal products (expt. 1). Heating of reactants in 1:1 ratios on the boiling water bath for up to 4 hours raises the yield of ethereal products and lowers the relative yield of phenolic compounds (expts. 2 and 3). More prolonged heating is accompanied by the usual phenomenon characteristic of this type of reaction: the yield of ethereal compounds falls and that of phenolics rises, since side by side with alkylation reactions we now get the reaction of isomerization of the alkyl phenolic ethers to alkyl phenols; the latter process is more significant the more easily the alkyl phenolic ethers isomerize.

Similar observations are made in the reaction with p-chlorophenol as shown in Table 2.

TABLE 2

Alkylation of p-Chlorophenol with 2-Pentene in Presence of $BF_3 \cdot O(C_2H_5)_2$

No. of expt.	Taken for reaction				Molar ratios of Chlorophenol to 2-pentene	Conditions of reactions		Products obtained					
	p-Chlorophenol (in g)	2-Pentene (in g)	$BF_3 \cdot O(C_2H_5)_2$			Temp.	Duration (in hrs)	Ethereal type			Phenolic type		
			(in g)	(in %)				in g	in %**	b.p.	in g	in %**	b.p.
1	12.45	7.80	1.35	6.8	1:1	95-97°	4	7.50	37.04	125-165° (9 mm)	2.30	11.36	121-140° (9 mm)
2	12.10	6.40	1.30	7.0	1:1	95-97	8	5.80	31.35		4.15	22.43	
3	12.30	3.90	1.45	8.9	2:1	95-97	4	5.25	47.51		—	—	

Interaction of o-chlorophenol with 2-pentene in 1:2 ratio for 4 hours at the temperature of the boiling water bath raises the yield of both the ethereal and the phenolic products (expt. 5, Table 1) in comparison with the reaction of components in 1:1 ratio. In these conditions o-chlorophenol almost completely enters into reaction and the total yield of products of alkylation is 66%. With a 2:1 ratio of chlorophenols to 2-pentene (expt. 6, Table 1; expt. 3, Table 2) the 2-pentene reacts quantitatively but the phenols are recovered to a considerable extent. At the same time in the reaction with o-chlorophenol the yield of ethereal products is much lower than in the same conditions in the reaction with p-chlorophenol.

Identification of products of alkylation. Sec.-amyl ethers of o- and p-chlorophenols, also sec.-amyl-substituted o- and p-phenols have not been described in the literature. For this reason the widely boiling fractions of ethereal and phenolic products were mixed and again fractionated into narrower fractions.

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* In expts. 1, 3, and 6 the yield was calculated on the 2-pentene; in all other experiments on the total sum of components.

** Yield calculated on total sum of components in expt. 1 and on 2-pentene in experiments 2 and 3.

In this way the following compounds were isolated.

1. Sec-amyl-o-chlorophenol. Colorless mobile liquid with a faint odor of o-chlorophenol; b.p. 137-140° at 11 mm.

d_4^{21} 1.0821; n_D^{21} 1.5250; MR_D 56.24; calculated 55.79.

10.61 mg sub.: 25.77 mg CO_2; 7.13 mg H_2O. 9.98 mg sub.: 24.12 mg CO_2; 6.95 mg H_2O. 0.1918 g sub.: 0.1384 g AgCl. Found %: C 66.28, 65.96; H 7.52, 7.73; Cl 17.85. $C_{11}H_{15}OCl$. Calculated %: C 66.47; H 7.61; Cl 17.86.

2. Sec-amyl ether of sec-amyl-o-chlorophenol. Colorless liquid with a pleasant odor; b.p. 121-124° at 10 mm.

d_4^{21} 0.9914; n_D^{21} 1.5010; MR_D 79.81; calculated 79.00.

11.77 mg sub.: 30.95 mg CO_2; 9.50 mg H_2O. 8.49 mg sub.: 22.32 mg CO_2; 6.99 mg H_2O. 0.1392 g sub.: 0.0757 g AgCl. Found %: C 71.78, 71.74; H 9.02, 9.23; Cl 13.45. $C_{16}H_{25}OCl$. Calculated %: C 71.46; H 9.38; Cl 13.20.

3. Sec-amyl ether of disec-amyl-o-chlorophenol. Colorless liquid with a pleasant odor; b.p. 140-144° at 10 mm.

d_4^{21} 0.9854; n_D^{21} 1.5052; MR_D 102.00; calculated 102.09.

11.32 mg sub.: 30.54 mg CO_2; 9.68 mg H_2O. 9.19 mg sub.: 24.81 mg CO_2; 7.93 mg H_2O. 25.952 mg sub.: 0.392 ml 0.02 N $AgNO_3$. 29.127 mg sub.: 0.442 ml 0.02 N $AgNO_3$. Found %; C 73.62, 73.68; H 9.59, 9.66; Cl 10.72, 10.78. $C_{21}H_{35}OCl$. Calculated %: C 74.39; H 10.42; Cl 10.47.

4. Sec-amyl-p-chlorophenol. Colorless mobile liquid. Crystallized overnight m.p. 51°, b.p. 130-131° at 8 mm; n_D^{20} 1.5308.

3.795 mg sub.: 9.340 mg CO_2; 2.950 mg H_2O. 6.400 mg sub.: 15.825 mg CO_2; 4.880 mg H_2O. 0.1659 g sub.: 0.1220 g AgCl. Found %: C 67.17, 67.30; H 8.69, 8.53; Cl 18.19. $C_{11}H_{15}OCl$. Calculated %: C 66.47; H 7.61; Cl 17.86.

5. Sec-amyl ether of o-sec-amyl-p-chlorophenol. Liquid with pleasant odor; b.p. 147-152° at 10 mm.

d_4^{20} 0.9895; n_D^{20} 1.4970; MR_D 79.47; calculated 79.00.

4.555 mg sub.: 12.085 mg CO_2; 3.775 mg H_2O. 5.125 mg substance: 13.565 mg CO_2; 4.230 mg H_2O. 0.1565 g substance: 0.0794 g AgCl. Found %: C 72.40, 72.23; H 9.27, 9.23; Cl 12.55. $C_{16}H_{25}OCl$. Calculated %: C 71.46; H 9.38; Cl 13.20.

In addition to the compounds described, the reaction with o-chlorophenol also gave a product with b.p. 165-166° at 10 mm (d_4^{21} 0.9334; n_D^{21} 1.5012), whose chlorine content was 5.1% (Carius). It was a fairly viscous, yellow liquid with a pleasant odor. Its composition was not established.

Consequently, with the help of boron fluoride etherate in the above-described conditions it is possible to introduce two alkyl groups into the benzene ring, already containing one substituent atom in the o- or p-position. It is a striking fact that the phenolic products isolated included only one sec-amyl-o-chlorophenol and one sec-amyl-p-chlorophenol. The sec-amyl ethers of chlorophenols were not isolated in sufficient quantity for identification.

SUMMARY

A study was made of the alkylation of o- and p-chlorophenols with 2-pentene, a by-product of the production of synthetic rubber by the Lebedev process, in presence of boron fluoride etherate.

The following were prepared and characterized: sec-amyl-o-chlorophenol; sec-amyl ether of sec-amyl-o-chlorophenol; sec-amyl ether of disec-amyl-o-chlorophenol; sec-amyl-p-chlorophenol; and sec-amyl ether of o-sec-amyl-p-chlorophenol.

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Received May 23, 1953

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the Voronezh State University

In this way the following compounds were isolated.

1. [illegible]. [illegible] b.p. [illegible] at [illegible] mm.

[illegible]

[illegible]. Found %: C [illegible], H [illegible], Cl [illegible]. [illegible]. Calculated %: [illegible]

Cl 15.88.

2. [illegible]. [illegible], b.p. [illegible] at [illegible] mm.

d_4^{20} [illegible]; n_D^{20} [illegible]; MR$_D$ [illegible]; calculated [illegible].

[illegible]. Calculated %: [illegible]

Cl 12.39.

3. [illegible]. Colorless liquid with a pleasant odor; b.p. [illegible] at [illegible] mm.

d_4^{20} [illegible]; n_D^{20} [illegible]; MR$_D$ [illegible]; calculated [illegible].

[illegible]

[illegible]. Found %: C [illegible], H [illegible]. [illegible]

Cl 16.79 [illegible]. Calculated %: C [illegible], H [illegible], Cl [illegible].

4. [illegible]. Colorless liquid [illegible] b.p. [illegible]

[illegible]

[illegible]. Found %: C [illegible], H [illegible], Cl [illegible]. [illegible]. Calculated %: C [illegible]

H 7.65, Cl 17.84.

5. [illegible]. Liquid with a pleasant odor; b.p. [illegible] at [illegible] mm.

d_4^{20} [illegible]; n_D^{20} [illegible]; MR$_D$ [illegible]; calculated [illegible].

[illegible]. Calculated %: [illegible]

[illegible] Cl 13.79.

[illegible] liquid with a pleasant odor. The compounds [illegible].

[illegible], with the help of [illegible] [illegible] [illegible] [illegible] [illegible] [illegible]

SUMMARY

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LITERATURE CITED

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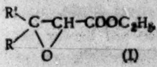
Received May 22, 1953

COMPOUNDS CONTAINING A THREE-MEMBERED OXIDE RING

VII. REACTION OF β, β-DIMETHYLGLYCIDAMIDE WITH CYCLOHEXYL-, DICYCLOHEXYL- AND BENZYLAMINES

V. F. Martynov

In previous communications devoted to the reaction of addition of aromatic amines to glycidic acids of the formula (I) where R and R' are aliphatic radicals, we established that in this case the rupture of the oxide ring of the glycidic acid takes place on the side of the tertiary carbon atom. The compounds resulting from this are α-hydroxy-β-arylamino-derivatives of the corresponding fatty acids. We arrived at this conclusion because these compounds lose carbon monoxide when treated with strong sulfuric acid, this being a well-known property of α-hydroxy acids. The second component of such a decomposition is bound to be the corresponding α-aminoaldehydes; however, we never obtained the latter, their place being taken in every case by the corresponding indole homologs. In the conditions of this reaction the α-aminoaldehydes which must have been formed would evidently undergo further transformations leading ultimately to an indole structure. A scheme for this transformation was submitted in the preceding communication [1]. In a certain sense, however, this scheme was hypothetical, in that we did not isolate a single one of the intermediate products that we proposed. Of course, we can here only speak of the separation of an aminoaldehyde, for the remaining intermediate compounds cannot be stable in presence of hot, strong sulfuric acid.

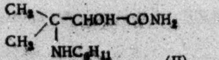


(I)

We resolved to demonstrate the validity of this scheme, i.e. to isolate the aminoaldehyde formed in this reaction. For this purpose it was necessary to exclude the possibility of secondary transformations of the aldehyde group. This could be done by replacing the aromatic amine by some aliphatic amine. As the latter we selected cyclohexylamine because it satisfied these requirements and, moreover, in size of molecule it was closest to aniline, which offered us the possibility of approaching most closely to the structure of the investigated compounds. Another advantage of this choice was that the aminoaldehyde which we might obtain in this case would inevitably be poorly soluble in water so that its isolation would be greatly facilitated.

Reaction of β,β-dimethylglycidamide with cyclohexylamine was effected by heating equimolecular amounts of these components in solution in absolute alcohol at 120-130°. The reaction gave a crystalline compound whose analysis identified it as the amide of hydroxycyclohexylamino-isovaleric acid.

By analogy with compounds that we had previously studied, the structure of this compound must be represented by formula (II). Treatment with strong sulfuric acid actually resulted in evolution of carbon monoxide which confirmed our proposed structure. However, this decomposition took place at a much higher temperature than we had observed for the corresponding compounds containing the residue of an aromatic amine. Whereas, for example, the ethyl ester of α-hydroxy-β-(p-toluidino)-isovaleric acid started to give off carbon monoxide at 110° [1], the compound here described only gave off carbon monoxide at 170-180°.



(II)

Rise of basicity of the amine leads to strengthening of the bond between the carboxyl and the α-carbon atoms. In this connection it is interesting to compare the decomposition of tert-butylglycolic acid with sulfuric acid. The structure of this compound is very similar to that of the hydroxyamino acids now under consideration but differs in that in place of an amino group there is a methyl radical and the latter, as we know, has an electronic shift opposite to that of the ammonium ion[*]. We might, thus, expect tert-butylglycolic acid to be decomposed by sulfuric acid in milder conditions. Indeed, it does decompose when heated to only 50° [2].

Consequently, the stability of α-hydroxy acids may be correlated with the inductive effect of the group in the β-position. The more pronounced the I-effect of these groups, the more stable will be the α-hydroxy acid. In respect of their stability, the compounds in question may be arranged in the following order:

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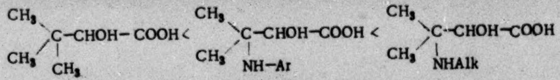
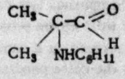
[*] Here we must remember that the amino group does not function here in its free state, but in the form of the ammonium ion, since the reaction takes place in a medium of sulfuric acid.



$(CH_3)_2C(CH_3)-CHOH-COOH < (CH_3)_2C(NH-Ar)-CHOH-COOH < (CH_3)_2C(NHAlk)-CHOH-COOH$

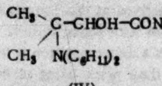
The second fragment of molecule obtained on decomposition by sulfuric acid of the amide of α-hydroxy-β-hexylamino-isovaleric acid was a liquid with a pronounced aliphatic amine odor. This compound gave a silver mirror and a crystalline derivative with 2,4-dinitrophenylhydrazone. The analytical data showed that we had indeed obtained α-cyclohexylamino-isobutyraldehyde (III). Thus our proposed scheme obtained one more proof of its validity.

Reaction of β,β-dimethylglycidamide with dicyclohexylamine was effected by a method similar to that already described. We obtained a crystalline compound to which, by analogy with the one described above, we attributed the formula of α-hydroxy-β-dicyclohexylamino-isovaleramide (IV). Under the action of strong sulfuric acid this compound likewise underwent decomposition, but the reaction proceeded at the very limit of decomposition of compounds with hydrochloric acid (above 180°) and therefore a very small amount of the corresponding aldehyde could be isolated, and the only evidence we obtained of its aldehydic character was the silver mirror.



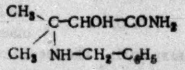
$(CH_3)_2C(NHC_6H_{11})-CHO$

(III)



$(CH_3)_2C(N(C_6H_{11})_2)-CHOH-CONH_2$

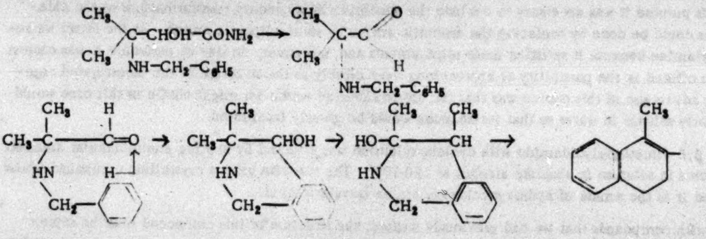
(IV)



$(CH_3)_2C(NH-CH_2-C_6H_5)-CHOH-CONH_2$

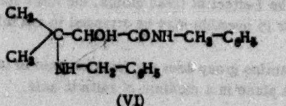
(V)

The product of addition of benzylamine to β,β-dimethylglycidamide that we obtained under the action of strong sulfuric acid underwent decomposition at 170-180° with loss of carbon monoxide. This behavior coupled with the analytical data enabled us to ascribe to it the formula of α-hydroxy-β-benzylamino-isovaleramide (V). In this case, however, no compound could be isolated, apart from CO, by the action of concentrated sulfuric acid; when the solution was made alkaline, no emulsion of basic compound was formed, although here we might have expected the formation of a dimethylated dihydroisoquinoline



This might be explained either by complete decomposition of the formed substance (which is highly improbable since the corresponding aminoaldehyde had been isolated when α-hydroxy-β-hexylamino-isovaleramide was decomposed in the same conditions) or, what is more probable, by sulfonation of the dimethyldihydroisoquinoline which might have been formed. Sulfonation could easily have proceeded at the given temperature of decomposition, and sulfonic acids as a rule dissolve readily in water at any pH, thus accounting for our failure to isolate any compound after making the solution alkaline.

We then prepared the free acid from α-hydroxy-β-benzylamino-isovaleramide. The amino group was removed with barium hydroxide. Benzylamine was also reacted with the ethyl ester of β,β-dimethylglycidic acid and gave a compound to which, by analogy with those described above, was ascribed the formula of the benzylamide of α-hydroxy-β-benzylamino-isovaleric acid (VI).



$(CH_3)_2C(NH-CH_2-C_6H_5)-CHOH-CONH-CH_2-C_6H_5$

(VI)

EXPERIMENTAL

Preparation of α-Hydroxy-β-cyclohexylamino-isovaleramide

5 g β,β-dimethylglycidamide and 4.3 g cyclohexylamine were dissolved in 30 ml absolute ethyl alcohol and sealed into an ampoule which was heated for 6 hours at 120°. Crystals separated on cooling and after crystallization from 30-40% alcohol melted at 164-165°. Yield 5 g (54%).

0.1028 g sub.: 12 ml N_2 (22°, 760.8 mm). 0.0990 g sub.: 11.4 ml N_2 (22°, 760.8 mm). Found %: N 13.15, 13.03. $C_{11}H_{22}O_2N_2$. Calculated %: N 13.08.

Preparation of α-Cyclohexylamino-isobutyraldehyde

5 g α-hydroxy-β-cyclohexylamino-isovaleramide was placed in 20 ml strong sulfuric acid. The mixture was heated with frequent shaking over a bare flame (thermometer in liquid). At 160° gas bubbles (carbon monoxide) started to come off and the liquid darkened. At 180° copious gas evolution started and the odor of sulfur dioxide was pronounced. Heating was concluded without waiting for complete cessation of gas evolution. The hot, dark liquid was poured onto ice, the solution then being only weakly colored. On neutralizing with sodium carbonate and, toward the end, with KOH solution, an emulsion was formed which was distilled with steam. The compound was extracted from the water with ether. The ethereal extract was dried, the ether driven off and the residue distilled in vacuum. Yield 1.6 g (41%) of light-yellow liquid with b.p. 84-87° at 4 mm. The substance had a definite fatty amine odor and gave a silver mirror.

$n_D^{18.5}$ 1.4677; $d^{18.5}$ 0.9385; MR_D 50.02. $C_{10}H_{19}ON$. Calculated: MR_D 49.79.

With 2,4-dinitrophenylhydrazine a precipitate was obtained which contained a sulfuric acid residue linked like a salt with the amino group of the aldehyde. Due to this structure, the dinitrophenylhydrazone was fairly highly soluble in aqueous alcohol.

The sulfuric acid residue was removed by dissolving the 2,4-dinitrophenylhydrazone of the aminoaldehyde in aqueous alcohol and adding to the solution an aqueous solution of sodium acetate. A copious precipitate of hydrazone at once came down. M. p. 153-154°.

0.0631 g sub.: 11.2 ml N_2 (22°, 761.5 mm). 0.0790 g sub.: 14.1 ml N_2 (22°, 761.5 mm). Found %: N 20.25, 20.36. $C_{16}H_{23}O_4N_5$. Calculated %: N 20.06.

The aldehyde crystallized after standing for a few days; apparently a trimer was obtained; m.p. 114-115° after recrystallization from ligroine.

Preparation of α-Hydroxy-β-dicyclohexylamino-isovaleramide (with E. S. Varshavskaya)

9 g β,β-dimethylglycidamide was dissolved in 20 ml absolute ethyl alcohol and the solution mixed with 16 g dicyclohexylamine. The mixture was sealed into an ampoule and heated for 6 hours at 120°. A dark, viscous liquid was obtained which crystallized after a few days. Yield 10 g crude product or 45% of the theoretical. After repeated recrystallization from 30% aqueous alcohol the m.p. was 113.5-114°.

0.1037 g sub.: 8.6 ml N_2 (17°, 760.2 mm). 0.1054 g sub.: 8.5 ml N_2 (17°, 760.2 mm). Found %: N 9.68, 9.42. $C_{17}H_{32}O_2N_2$. Calculated %: N 9.6.

Decomposition of α-hydroxy-β-dicyclohexylamino-isovaleramide under the action of strong sulfuric acid. 2 g of the amide was placed in 10 ml strong sulfuric acid. The amide went into solution on heating. At 180° gas began to come off with a strong odor of sulfur dioxide. The solution darkened considerably. Without waiting for cessation of gas evolution, the mixture was poured onto ice. After neutralization, the dark solution was distilled with steam and in the distillate collected a few drops of substance with the distinct odor of an aliphatic amine and which gave a good silver mirror.

Interaction of β,β-Dimethylglycidamide with benzylamine (with Z. M. Gofung)

10 g of the amide in 30 ml absolute ethyl alcohol was heated with 9 g benzylamine in a sealed tube at 130° for 9 hours. Crystals of the amide of α-hydroxy-β-benzylamino-isovaleric acid separated on cooling. Yield 10 g (52%). After recrystallization from water the m.p. was 90-91°.

0.1062 g sub.: 12 ml N_2 (18°, 745 mm). 0.1005 g sub.: 11.3 ml N_2 (18°, 744 mm). 0.0216 g sub.: 0.1141 g camphor: Δt 36°. 0.0112 g sub.; 0.1637 g camphor: Δt 13°. Found %: N 12.82, 12.73; M 211.3, 210.7. $C_{12}H_{18}O_2N_2$. Calculated %: N 12.61; M 222.0.

Preparation of α-Hydroxy-β-benzylamino-isovaleric Acid

1.5 g amide of α-hydroxy-β-benzylamino-isovaleric acid was heated in a round bottomed flask under a reflux condenser with 2.6 g barium hydroxide in 25 ml water for 8 hours. The barium was precipitated with sulfuric acid removed with barium carbonate. The precipitate of barium sulfate was filtered off and the filtrate evaporated in vacuum to a small volume. A fine crystalline mass appeared after standing for 2 days in a vacuum desiccator and had m.p. 70-71° after recrystallization from water. Yield 0.25 g or 16.6% of the theoretical yield.

0.0935 g substance: 5.2 ml N_2 (22°, 764 mm). 0.0867 g substance: 4.8 ml N_2 (22°, 764 mm). Found %: N 6.37, 6.33. $C_{12}H_{17}O_3N$. Calculated %: N 6.27.

Interaction of Ethyl β,β-Dimethylglycidate with Benzylamine

10 g ethyl β,β-dimethylglycidate was heated in a sealed tube with 15 g benzylamine and 25 ml ethyl alcohol to 150-160° for 9 hours. After this period the ethyl alcohol was removed in vacuum, leaving in the flask a light-brown resinous mass which did not crystallize after standing for two days. A portion of this mass was treated with steam and then dried in a vacuum-desiccator. In this manner crystals of the benzylamide of α-hydroxy-β-benzylamino-isovaleric acid were formed and had m.p. 88-89° after three recrystallizations from ligroine.

0.0851 g substance: 6.9 ml N_2 (22°, 749 mm). 0.0697 g substance: 5.5 ml N_2 (22°, 766 mm). 0.0685 g substance: 15.16 g benzene: Δt 0.08°. 0.0850 g substance; 17.1 g benzene: Δt 0.09°. Found %: N 9.09, 9.05; M 290.4, 285.0. $C_{19}H_{24}O_2N_2$. Calculated %: N 8.97; M 312.0.

Hydrochloride of the Benzylamide of α-Hydroxy-β-Benzylamino-Isovaleric Acid

This was prepared from the second portion of resinous mass left in the flask (see above) by the action of concentrated hydrochloric acid. The salt was twice recrystallized from ethyl alcohol; m.p. 228°.

0.4400 g substance: 24.7 ml 0.1 N H_2SO_4. 0.4735 g substance: 25.4 ml 0.1 N H_2SO_4. Found %: N 7.72, 7.85. $C_{19}H_{25}O_2N_2Cl$. Calculated %: N 8.05.

SUMMARY

1. The reaction of β,β-dimethylglycidamide with cyclohexyl-α, dicyclohexyl-β and benzylamines was investigated. The following compounds which have not been described in the literature were obtained: α-Hydroxy-β-cyclohexylamino-isovaleramide; α-hydroxy-β-dicyclohexylamino-isovaleramide; α-hydroxy-β-benzylamino-isovaleramide; the benzylamide of α-hydroxy-β-benzylamino-isovaleric acid; α-hydroxy-β-benzylamino-isovaleric acid; α-cyclohexylamino-isobutyraldehyde.

2. The possibility of transition from glycidic acids to α-aminoaldehydes was exemplified by the preparation of α-cyclohexylamino-isobutyraldehyde from β,β-dimethylglycidamide.

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* See Consultants Bureau Translation, page 1047.

COMPOUNDS CONTAINING A THREE-MEMBERED OXIDE RING

VIII. REACTION OF ETHYL β,β-TETRAMETHYLENEGLYCIDATE WITH ANILINE

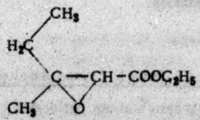
V. F. Martynov

We have investigated the addition of aromatic amines to glycidic acids with reference to the ethyl esters of β,β-dimethyl and β-methyl-β-ethylglycidic acids [1, 2].

Rupture of the oxide ring of these glycidic acids under the action of aromatic amines took place always at the same point, namely from the side of the tertiary carbon atom; however, the speed of addition of aromatic amines changes abruptly on passing from β,β-dimethyl- to β-methyl-β-ethylglycidic acid.

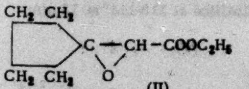
Whereas heating for 6 hours was sufficient for ethyl β,β-dimethylglycidate with aromatic amines of the type of aniline or p-toluidine in order to obtain a satisfactory yield [1], for ethyl-β-methyl-β-ethylglycidate (I) the same yield could only be obtained under otherwise identical conditions after heating for 40 hours [2].

This illustrated the great steric hindrance due to the introduction of another methyl group into the compound. Due to the free rotation along the axis of the carbon-carbon bond, the methyl group of the ethyl radical is suspended, as it were, over the oxide ring and thereby hinders the approach of reactants to the ring. In this connection it was interesting to investigate the addition of aromatic amines to those glycidic acids in which substituents in the β-position were linked to the ring and were thereby either deprived completely of the ability to change their position in space or only possessed very limited mobility. Special interest is attached in this respect to β,β-tetramethyleneglycidic acid (II) in which, due to the planar structure of the five-membered ring, substituents at the tertiary carbon atom are at the maximum distance from the oxide ring. It might therefore be expected that the addition of aromatic amines would proceed much more intensively than in the case of β,β-dimethyl- and β-methyl-β-ethylglycidic acids notwithstanding that in the latter the volume of substituents in the β-position is smaller than in β,β-tetramethyleneglycidic acid.



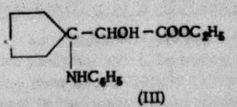
(I)

We carried out an investigation with ethyl β,β-tetramethyleneglycidate which we prepared by condensation of cyclopentanone with ethyl chloroacetate in toluene solution in presence of metallic sodium. This method requires less time and gives a higher yield than the condensation with sodium ethylate [3]. We performed the interaction with an aromatic amine (aniline) by the usual method of heating the glycidic ester with three times the amount of aniline in a sealed tube at 170-180°. It was found that in this case the addition of aniline takes place more energetically than with either of the two esters of glycidic acid mentioned above. Heating for 8 hours led to nearly quantitative yield of addition product. Thus, the above-mentioned considerations are actually relevant.

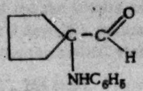


(II)

Concerning the point of rupture of the oxide ring of glycidic acid under the action of aniline, we established it by our previously applied method [1, 2]. Treatment of the addition product with concentrated sulfuric acid with heating resulted, even at 110°, in commencement of vigorous evolution of gas bubbles (carbon monoxide); no resinification whatever was observed, and the solution acquired faint yellow color. This behavior permitted us to claim with a high degree of probability that we were dealing with the ethyl ester of α-hydroxy-β-anilino-β,β-tetramethylenepropionic acid (III), since only α-hydroxy acids split off carbon monoxide under the action of sulfuric acid.


(III)

For conclusive proof it would have been necessary to isolate the second fragment of the molecule which must consist of anilino-tetramethyleneacetaldehyde (IV). As we showed in previous communications, however [1, 2], these arylamino aldehydes are unstable in a medium of concentrated sulfuric acid and undergo further transformations to give the corresponding indole homologs. In the present case the amino aldehyde (IV) should be converted into tetrahydrocarbazole whose formation may be represented by the scheme: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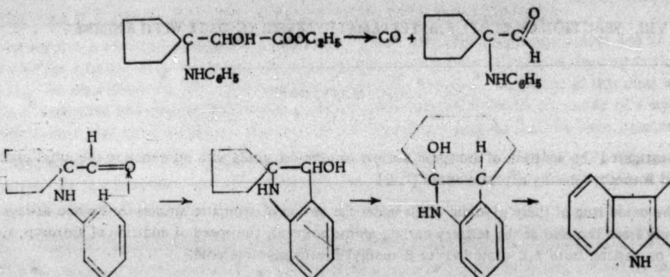

We obtained a quantitative yield of a crystalline substance whose melting point was actually that of tetrahydrocarbazole. It gave a picrate melting at the same temperature as tetrahydrocarbazole picrate. For conclusive proof of its structure we synthesized tetrahydrocarbazole by E. Fischer's method [4]. Mixed melting tests of the two compounds as well as of their picrates did not give a depression. Consequently, we have definitely established both the structure of the product of addition of aniline to ethyl β,β-tetramethyleneglycidate and the mechanism of transformation of anilino-tetramethyleneacetaldehyde. A retropinacolin rearrangement had here taken place with ring expansion.

EXPERIMENTAL

Synthesis of Ethyl Tetramethyleneglycidate

This synthesis was not performed by the literature procedure [3]. A mixture of 73 g cyclopentanone and 120 g ethyl monochloroacetate was added with intensive stirring to 20 g finely powdered sodium in toluene. In order to initiate the reaction the addition of the mixture to the sodium was carried out at the ordinary temperature, but as soon as a temperature rise was observed the flask was immersed in ice and salt and the addition of the mixture of cyclopentanone and ethyl monochloroacetate was continued at such a rate that the temperature of the reaction mixture did not rise above +5°.

At the end of the reaction the contents of the flask had changed into a dark, gelatinous mass. On the following day, the reaction mass was decomposed with water, when the dark color disappeared.

The toluene extract was dried with sodium sulfate. The reaction product distilled at 113-114° at 13 mm. Yield 71 g (50%). The literature method gave 41% [3].

Reaction of Ethyl Tetramethyleneglycidate with Aniline

A mixture of 20 g ethyl tetramethyleneglycidate and 30 g aniline (three times the amount of aniline) was sealed into a glass ampoule and heated for 8 hours at 170-180°. At the conclusion of heating the ampoule was left overnight; the contents crystallized. The crystals were pressed and recrystallized 4 times from ligroine to give 20 g white, silky needles (65%). Allowing for the unavoidable losses during 4 crystallizations, we may estimate the yield at 80-90%. M.p. 117-118°.

0.1350 g substance: 6.5 ml N_2 (20°, 759.5 mm). 0.1685 g substance: 7.7 ml N_2 (20°, 756 mm). Found %: N 5.53, 5.23. $C_{15}H_{21}O_3N$. Calculated %: N 5.32.

Reaction of Ethyl α-Hydroxy-β-anilino-β,β-tetramethyleneglycidate with Strong Sulfuric Acid

To 5 g substance was added 40 ml concentrated sulfuric acid. On heating, the substances mutually dissolved. At 110-120° intensive evolution of carbon monoxide was observed and the mixture acquired a faint yellow color.

After gas bubbles had ceased to come off at the indicated temperature range, the reaction mixture was poured onto ice; white crystals of tetrahydrocarbazole came down and were drained and washed with water; quantitative yield. M.p. 113-114° after recrystallization from aqueous alcohol.

0.0976 g substance: 6.9 ml N_2 (18°, 759 mm). Found %: N 8.1. $C_{12}H_{13}N$. Calculated %: N 8.2.

Other authors give m.p. 110 to 120° [4, 5]. Authentic tetrahydrocarbazole which we synthesized by Fischer's method also melted at 113-114°.

The picrate obtained from both tetrahydrocarbazoles melted at 144-145°. In both cases the mixed melting test did not give a depression.

SUMMARY

1. The reaction between ethyl tetramethyleneglycidate and aniline was investigated. It was established that the oxide ring of this ester is ruptured at the side containing the tertiary β-carbon atom.

2. A new method of synthesis of tetrahydrocarbazole was developed.

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* See Consultants Bureau Translation, page 1637.

CONFIGURATION AND PROPERTIES

OF UNSATURATED ACIDS AND THEIR DERIVATIVES

THE REACTIVITY OF ESTERS OF OLEIC AND ELAIDIC ACIDS

E. G. Maleeva

In a study of the reactivity of oleic and elaidic acids [1] it was found that the differing reactivities of these stereoisomers is consistent with the theory of steric hindrance and confirms the theory that oleic and elaidic acids are respectively cis- and trans-isomers. It was also established that the methyl esters of oleic and elaidic acids are saponified (by alkali), hydrogenated and oxidized at different velocities. It was important to verify this observation for other derivatives of oleic and elaidic acids. It was also necessary to establish whether and to what extent the composition and structure of the alcohol radical influenced the reactions. Starting from these considerations, we have studied the reactivity of propyl oleate, isopropyl oleate, butyl oleate and benzyl oleate, also their geometrical isomers prepared from elaidic acid.

Experiments on saponification, hydrogenation and oxidation were carried out in the conditions previously described by us in work with methyl oleate and methyl elaidate; in this connection it transpired that saponification with alcoholic alkali of all the oleates, like that of methyl oleate, proceeds rather more slowly than in the case of the corresponding elaidates. On the other hand, oleates are hydrogenated and oxidized more quickly than elaidates.

Consequently, the experimental data indicate that the space round the ester groups of oleates is blocked to some extent by the hydrocarbon radical $CH_3(CH_2)_7$, which hinders access to it of the alkali elements. This is apparently not the case with elaidates, and their saponification therefore proceeds more quickly. From this standpoint the results of experiments on saponification confirm the cis-structure of oleates and the trans-structure of elaidates.

This conclusion becomes even more convincing when we consider the results of hydrogenation and oxidation of oleic and elaidic acids and their esters.

Concerning the role of the alcohol radical as a factor creating steric hindrance, we succeeded in observing relatively little difference between the reactivities of the benzyl esters. Here the benzyl group appears to retard saponification to a greater extent than any other alcoholic group in the esters that we studied.

Reactions at the double bond proceed rather more slowly with benzyl elaidate than in the other elaidates.

EXPERIMENTAL

1. Synthesis of esters of oleic and elaidic acids. Propyl oleate was prepared from silver oleate (1 mole) and propyl bromide (4 moles). A mixture of the salt and the bromide was first shaken for 3 hours and then heated for 30 minutes on a boiling water bath under a reflux condenser. At the conclusion of the reaction the mixture was diluted with dry ether, filtered and fractionally distilled. The ester was a light yellow liquid without odor; b.p. 220-220.5° (13 mm). d^{15} 0.8699.

Isopropyl oleate. Light-yellow with b.p. 218° (16 mm), d^{15} 0.8678 was prepared analogously to the above from silver salt and isopropyl bromide.

Butyl oleate was prepared in the form of a colorless liquid (similar to the above) by heating the components for 5 hours at 110° on an oil bath under a reflux condenser. B.p. 225-226° (15 mm), d^{16} 0.8670.

Benzyl oleate was synthesized from oleic acid (1 mole) and benzyl alcohol (3 moles) in presence of sulfuric acid. The mixture was heated for 8 hours on a boiling water bath; after washing with water, the product was dissolved in ether, neutralized with alcoholic KOH and carefully washed with water until free from alkali. Benzyl oleate distilled in vacuum at 235-239° (6-7 mm). A light-yellow oil, b.p. 216-218° (1 mm), d_4^{23} 0.9315, n_D^{23} 1.4820. At 23° it dissolves in 5 parts alcohol.

Propyl elaidate. From the Ag salt of elaidic acid and propyl bromide; b.p. 217° (12 mm), d^{15} 0.8710.

Isopropyl elaidate. From the Ag salt and isopropyl bromide, b.p. 218° (15 mm), d^{15} 0.3671.

Butyl elaidate. From the Ag salt and butyl bromide, b.p. 228° (14 mm), d^{16} 0.8671.

Benzyl elaidate was prepared in a similar manner to benzyl oleate. A light-yellow, oily liquid, b.p. 227-229° (1 mm), d^{23} 0.9372, n_D^{23} 1.4840. Less soluble than benzyl oleate in alcohol.

2. Saponification with alcoholic alkali. Saponification of each pair of isomeric esters was effected simultaneously in two identical vessels fitted with platinum electrodes and well ground covers. To each vessel, containing a weighed amount of ester equivalent to 0.0005 mole, was added 2 ml 0.1 N alcoholic KOH. Temperature, 28°. The start of each experiment was taken as the instant of addition of the alkali; immediately afterwards the first determination of electrical conductivity of the solution was carried out; after another 30 minutes a second determination of electrical conductivity was carried out; after 90 minutes a third and after 150 minutes a fourth determination was carried out. In other respects the experimental procedure was the same as described in our previous communication [2]. In Table 1 are set forth the results of observations of the rate of saponification of the esters from the change in electrical conductivity whose fall in the present case depends on the fall in concentration of the hydroxyl ions consumed in saponifying the ether.

TABLE 1

Compound	Change of electrical conductivity			
	time (in minutes)			
	0	30	90	150
Propyl oleate. . .	571	534	514	515
Propyl elaidate. .	561	515	492	487
Isopropyl oleate .	571	537	515	512
Isopropyl elaidate	564	548	495	487
Butyl oleate. . . .	571	534	520	520
Butyl elaidate. . .	564	512	495	492
Benzyl oleate . . .	571	540	526	526
Benzyl elaidate .	563	512	500	487

3. Hydrogenation of esters of oleic and elaidic acids. Results of similar experiments have already been published but were carried out in other conditions [3]. The results here presented are also supplemented by data for hydrogenation of the benzyl esters.

The esters were hydrogenated in presence of platinum supported on $BaSO_4$; materials used in each experiment were 0.25 g $BaSO_4$ with 0.008 g Pt, 15 ml ethyl alcohol and 0.005 mole of the ester.

All experiments were performed at 28° in a hydrogenation apparatus, experiments with two isomeric esters being run side by side (Table 2).

TABLE 2

Compound	Amount of hydrogen added (in ml)		
	20 min.	40 min.	60 min.
Propyl oleate. . . .	45	80	103
Propyl elaidate . .	37	73	92
Isopropyl oleate . .	45	79	104
Isopropyl elaidate.	38	73	90
Butyl oleate	44	80	104
Butyl elaidate. . .	38	72	86
Benzyl oleate . . .	40	65	100
Benzyl elaidate. .	32	72	80

TABLE 3

Compound	Change of electrical conductivity			
	duration (in minutes)			
	3	15	30	45
Propyl oleate	391	425	465	500
Propyl elaidate. . .	400	417	434	465
Isopropyl oleate . .	391	434	485	500
Isopropyl elaidate.	391	400	434	454
Butyl oleate	400	434	476	500
Butyl elaidate	400	417	434	466
Benzyl oleate	400	434	465	500
Benzyl elaidate . . .	391	417	444	444

4. Oxidation of esters of oleic and elaidic acids. We had already established that methyl oleate and methyl elaidate do not react equally easily with aqueous $KMnO_4$. In this investigation, therefore, we also evaluated the oxidation of the esters by the change of electrical conductivity of aqueous $KMnO_4$ [1].

Oxidation experiments were carried out simultaneously with equal weights of isomeric esters (1/1500 mole). To the weighed amount of ester was added 5 ml 1.5% aqueous $KMnO_4$; the first measurement of electrical conductivity was made after 3 minutes, the second after 15, the third after 30 and the fourth after 45 minutes. Temperature 27°. The data are set forth in Table 3.

Thanks are due to Prof. A. K. Plisov for valuable advice during this investigation.

SUMMARY

1. Benzyl oleate and benzyl elaidate were synthesized and their properties described.

2. It was established that in harmony with the theory of steric hindrance the oleates are saponified more slowly than the elaidates and are oxidized and hydrogenated more quickly than elaidates.

3. The reactions of saponification, oxidation and reduction of oleic and elaidic acids and their esters confirm the structure of these acids as cis- and trans-isomers respectively.

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* See Consultants Bureau English translation, page 69

** See Consultants Bureau English translation, page 71

SYNTHESIS OF 1,1-DIALKYLCYCLOPROPANES FROM ALDEHYDES

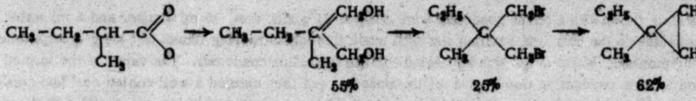
Ya. M. Slobodin, V. I. Grigoryeva and Ya. E. Shmulyakovsky

At the present time many hydrocarbons of the cyclopropane series are not readily accessible and have been inadequately investigated.

Below we describe the synthesis of 1-methyl-1-ethylcyclopropane and 1-methyl-1-isopropylcyclopropane which have not previously been prepared by a direct method.

Both hydrocarbons have been isolated from complex hydrocarbon mixtures formed by the action of zinc dust on 1,1,1-tribromotrimethylpropane and on 1,1,1-tribromotrimethyl-2-methylpropane [1]. The amount of these hydrocarbons in the mixtures resulting from dehalogenation is 3 and 5% respectively.

The starting material for synthesis of 1-methyl-1-ethylcyclopropane in our investigation was 2-methyl-1-butanal. Condensation of this aldehyde with formaldehyde in an alkaline medium gave a diol [2] which was converted with PBr_3 into the dibromide [3]. Cleavage of two bromines from the dibromide with zinc dust led to formation of the hydrocarbon.



The so-formed hydrocarbon was of satisfactory purity as shown by spectroscopic examination; it was not contaminated with unsaturated hydrocarbons. In the Raman spectrum of this hydrocarbon the cyclopropane ring was represented by the group of frequencies 850, 881, 934, 1236 and 3058 cm^{-1}.

The starting material for synthesis of 1-methyl-1-isopropylcyclopropane was 2,3-dimethyl-1-butanal which gave the required cycloparaffin by the same series of reactions.

The purity of the hydrocarbon was adequate. Spectroscopic examination showed it to be free from unsaturated hydrocarbons. Corresponding to the three-membered ring in the Raman spectrum of 1-methyl-1-isopropylcyclopropane were the frequencies 841, 849, 933, 1228, 1258, and 3063 cm^{-1}. Our method may be proposed as a general method of synthesis of 1,1-dialkylcyclopropanes.

EXPERIMENTAL

2-Methyl-2-ethylpropane-1,3-diol

The diol was prepared from 2-methylbutanal and formaldehyde [2]. In a three-necked flask fitted with stirrer, dropping funnel and reflux condenser was placed a solution of 17 g KOH in 75 ml alcohol. From the dropping funnel was slowly run in a mixture of 22 g 2-methylbutanal, 65 ml 28%, formaldehyde and 30 ml alcohol. During the addition of the mixture the temperature in the flask was kept at 40°. After completion of the addition, the flask was heated to 80°. Stirring was continued for 18 hours at this temperature. The alcohol was then driven off and the residue extracted 5-6 hours with ether. The ethereal solution was dried, the ether was driven off, and the diol was distilled. The latter formed white, hygroscopic crystals with m.p. 43° and b.p. 111-114° (10 mm). Yield of diol, 55% of the theoretical.

Found %: C 59.96; H 11.53. $C_6H_{14}O_2$. Calculated %: C 61.01; H 11.95

2-Methyl-2-isopropylpropane-1,3-diol

Preparation was by the above-described method, using 46.4 g 2,3-dimethylbutanal, 60 ml alcohol, 130 ml

28%, formaldehyde and a solution of 35 g KOH in 150 ml alcohol. Yield of diol, 46% of the theoretical. B.p. 139-140° (24 mm); m.p. 56-57°.

Found %: C 62.40; H 12.30; $C_7H_{16}O_2$. Calculated %: C 63.55; H 12.22

1,3-Dibromo-2,2-dialkylpropanes

Into a flask fitted with a dropping funnel and reflux condenser was charged 0.25 mole diol, after which 0.25 mole PBr_3 was run in slowly, the flask being cooled with iced water [3]. After the PBr_3 had been added, the bath temperature was slowly raised to 100°, and then the water bath was replaced by an oil bath and the mixture heated for 18 hours at 150°. After cooling, the mass was poured into cold water. The dibromo compound was extracted with ether. The ethereal solution was washed with water, then with sodium carbonate solution and again with water, and dried over calcium chloride. The ether was driven off and the dibromo compound distilled in vacuum.

1,3-Dibromo-2-methyl-2-ethylpropane. Yield 25% of the theoretical. B.p. 78° at 5mm and 92° at 17 mm.

d_4^{20} 1.6078; n_D^{20} 1.5073; MR_D 45.14. Calc. MR_D 45.47. Found %: Br 65.32. $C_6H_{12}Br_2$. Calculated %: Br 65.55.

Raman Spectrum

188 (2), 242 (3), 312 (1), 336 (0.5), 371 (1 w), 430 (2w), 444 (2 w), 501 (2), 595 (0.5), 636 (7), 655 (10). 695 (2), 736 (6), 778 (2), 826 (3), 858 (4), 888 (1 w), 928 (2), 999 (1), 1055 (1), 1172 (0.5), 1192 (0.5), 1263 (2), 1309 (0.5), 1341 (0.5), 1443 (0.5).

1,3-Dibromo-2-methyl-2-isopropylpropane. Yield 33% of the theoretical. B.p. 123-125° at 30 mm; d_4^{20} 1.5408; n_D^{20} 1.5073; MR_D 49.86. Calc. MR_D 49.89.

Found %: Br 62.25. $C_7H_{14}Br_2$. Calculated %: Br 62.01.

1-Methyl-1-ethylcyclopropane

Into a flask fitted with a reflux condenser were charged 31 g zinc dust, 45 ml alcohol and 5 ml water. The mixture was heated to the boil, and addition was then made through a dropping funnel of 14.5 g 1,3-dibromo-2-methyl-2-ethylpropane. Water at 70° was circulated through the reflux condenser. The vapor of the formed hydrocarbon passed without condensing through the reflux condenser and then entered a well-cooled coil and condensed in the receiver. The hydrocarbon was washed with water, dried over calcium chloride and distilled over sodium. Yield 62% of the theoretical.

B.p. 56.5-57°; d_4^{20} 0.7013; n_D^{20} 1.3888; MR_D 28.30.

C_6H_{12}. Calc. MR_D 28.40*.

Raman Spectrum

199 (0.5), 265 (0.5), 362 (1 w), 415 (1), 431 (1), 446 (1), 479 (4), 674 (10), 736 (1), 788 (1), 851 (1), 881 (6), 934 (7), 1000 (5), 1067 (4), 1115 (2), 1236 (3), 1285 (3), 1388 (1), 1435 (3), 1456 (3), 2933 (6), 2960 (6), 2994 (20), 3058 (5).

1-Methyl-1-isopropylcyclopropane

The hydrocarbon was prepared from 1,3-dibromo-2-methyl-2-isopropylpropane in the conditions described above. The reaction was carried out in a Wurtz flask; the hydrocarbon was progressively distilled off with the alcohol as formed. Loss of alcohol during the reaction was made good by addition from the dropping funnel. Yield 77% of theory.

B.p. 82°; d_4^{20} 0.7215; n_D^{20} 1.4000; MR_D 39.92; Calc. MR_D 40.02.

Found %: C 85.29; H 14.23. C_7H_{14}. Calculated %: C 85.62; H 14.38.

Raman Spectrum

271 (2w), 309 (2w), 348 (2), 372 (1), 392 (1), 489 (3), 501 (2), 649 (1), 663 (10), 715 (1), 778 (1W), 841 (8), 849 (5), 933 (9), 1004 (6), 1040 (2), 1084 (2), 1124 (4), 1158 (1), 1196 (2), 1228 (1), 1258 (7), 1313 (3), 1358 (2), 1390 (2), 1425 (3), 1448 (6), 1461 (6), 2874 (10), 2902 (2), 2936 (4), 2960 (8), 2995 (8), 3063 (3).

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* The increment for a three-membered ring is assumed to be 0.7.

SUMMARY

1-Methyl-1-ethylcyclopropane and 1-methyl-1-isopropylcyclopropane have been prepared for the first time by direct synthesis.

Data are given for the Raman spectra of the prepared hydrocarbons and the intermediate products of their synthesis.

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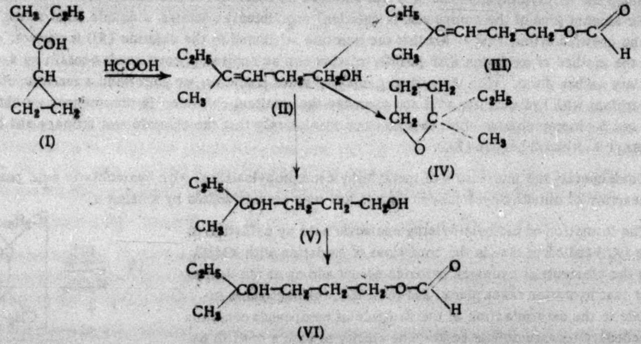
THE MECHANISM OF TRANSFORMATIONS OF TERTIARY ALCOHOLS OF THE CYCLOPROPANE SERIES UNDER THE INFLUENCE OF INORGANIC AND ORGANIC ACIDS

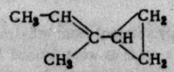
II. INTERACTION OF METHYLETHYLCYCLOPROPYLCARBINOL WITH DILUTE FORMIC ACID

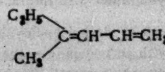
T. A. Favorskaya and N. V. Shcherbinskaya

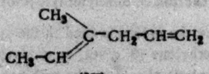
In collaboration with S. E. Chernobelskaya [1], we have studied the reaction of methylethylcyclopropylcarbinol with 80% formic acid; the sole product of this reaction was 2,2-methylethyltetrahydrofuran. In the present investigation we used more dilute acid in the dilution of 1:2 (pH 0.88) in order to have the possibility of obtaining intermediate products of the reaction and thus gaining an insight into its mechanism. The results that we obtained showed that in these conditions the interaction of methylethylcyclopropylcarbinol (I) with formic acid proceeds by the same mechanism as in the interaction of formic acid with dimethylcyclopropylcarbinol [2]: the hydroxyl group of the tertiary is shifted to the β-position while the three-membered ring is opened to form the unsaturated primary alcohol, 3-methyl-3-hexene-6-ol (II). This alcohol is then partly esterified with formation of the formic ester (III), partly isomerized to 2,2-methylethyltetrahydrofuran (IV), and to a small extent hydrogenated to α,α-methylethyltetramethylene glycol (V), which esterifies to the monoester (VI).



Moreover substitution of one methyl group of the alcohol by ethyl brings about still another direction of reaction —dehydration. This leads to formation of a mixture of hydrocarbons. The oxidation data showed that the mixture contains a cyclic hydrocarbon, dimethylcyclopropylethylene (VII), and also (apparently) the two isomeric unsaturated hydrocarbons (VIII) and (IX):


(VII)


(VIII)

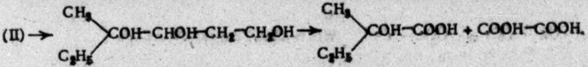

(IX)

Here, as in the case of dimethylcyclopropylcarbinol, the formed unsaturated alcohol and its ester undergo conversion into an azeotropic mixture with b.p. 162-167°. Since isomeric transformations are possible in the hydrolysis of the esters, the mixture of alcohol and ester was treated with MgICH_3 for establishment of its structure. The reaction products were decomposed with water and sulfuric acid, dried and distilled in vacuum to give a primary alcohol —3-methyl-3-hexene-6-ol; on carrying out the distillation at normal pressure, however, the alcohol isomerizes to

2,2-methylethyltetrahydrofuran. Decomposition of the reaction products with water alone followed by fractionation at the ordinary pressure gives the primary alcohol as the sole product. Negligible traces of sulfuric acid thus cause isomerization of the distilled alcohol to γ-oxide.

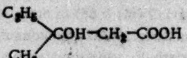
The yield of high-boiling fractions, corresponding to the glycol and its ester, is considerably lower than in the case of dimethylcyclopropylcarbinol; moreover, the formation of dienic hydrocarbons leads to polymeric products which contaminate the glycol and ester and still further reduce the yield. Hydrolysis of this mixture gave the glycol (V) in sufficiently pure form.

The mixture of alcohol (II) and ester (III) was oxidized with $KMnO_4$ solution; among other products of oxidation was found methylethylglycolic acid, whose formation may be represented by the scheme:



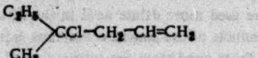
$$(II) \rightarrow (CH_3)(C_2H_5)COH{-}CHOH{-}CH_2{-}CH_2OH \rightarrow (CH_3)(C_2H_5)COH{-}COOH + COOH{-}COOH.$$

We obtained the same acid by oxidation of methylethylallylcarbinol and by oxidation of the unsaturated chloride formed from methylethylcyclopropylcarbinol by treatment with hydrochloric acid [3]. Oxidation of this chloride gave, apart from methylethylglycolic acid, methylethylethylenelactic acid (X). Methylethyl ketone was not obtained at all. The chloride was accordingly assumed to have the structure of 4-methyl-4-chloro-1-hexene (XI)



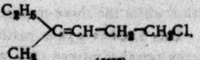
$$(C_2H_5)(CH_3)COH{-}CH_2{-}COOH$$

(X)



$$(C_2H_5)(CH_3)CCl{-}CH_2{-}CH{=}CH_2$$

(XI)



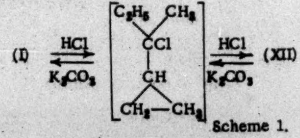
$$(C_2H_5)(CH_3)C{=}CH{-}CH_2{-}CH_2Cl.$$

(XII)

Since the methylethylglycolic acid was obtained by oxidation of two differently constituted compounds and since the alcohol (one of the compounds in question) undoubtedly contains a double bond at the tertiary carbon atom, the question arises, first, whether the structure attributed to the chloride (XI) is correct, and, second, whether the method of oxidation with $KMnO_4$ solution can be applied to compounds containing a double bond at the tertiary carbon atom. With the aim of clarifying these problems, we performed a reaction of methylethylcyclopropylcarbinol with hydrochloric acid and ozonized the resultant chloride. In this manner we obtained methylethyl ketone and β-chloropropionic acid, thus showing conclusively that the chloride was primary and had the structure of 3-methyl-6-chloro-3-hexene (XII).

Consequently the interaction of methylethylcyclopropylcarbinol with hydrochloric acid proceeds similarly to the reaction of dimethylcyclopropylcarbinol and may be represented by scheme 1.

The formation of methylethylethylenelactic acid by oxidation of chloride (XII) indicates that in the conditions of oxidation with $KMnO_4$ solution the elements of hydrogen peroxide do not add on at the double bond but that hydration takes place, and therefore, this method is inapplicable to the determination of the structure of compounds containing a secondary-tertiary double bond. The ability of such a bond to be hydrated, which is now explained, confirms the theory—enunciated by us in a previous communication—that the formation of α,α-dimethyltetramethylene glycol by interaction of dimethylcyclopropyl carbinol with formic acid proceeds through addition of water to 2-methyl-2-penten-5-ol at the double bond. Such an interpretation of the reaction mechanism may also be applied to the formation of α,α-methylethyltetramethyleneglycol which is prepared by reaction of methylethylcyclopropylcarbinol with formic acid.



Scheme 1.

Since the iodide formed in the synthesis of methylethylcyclopropylcarbinol from ethylmagnesium iodide and acetyltrimethylene [3] gives, on oxidation with permanganate, the same acids as were formed from the chloride, while hydrolysis also gives the original cyclic alcohol, it is clear that the iodide is not 3-methyl-3-iodo-1-hexene, but a primary iodide with the structure of 3-methyl-6-iodo-1-hexene.

The action of organic acids on tertiary alcohols of the cyclopropane series results in the first place in formation of primary alcohol which then forms an ester; hence it may be suggested that the first step in the reaction with hydrogen halides is also formation of an unsaturated alcohol whose hydroxyl is then replaced by chlorine. In attempting, however, to prepare chloride (XI) by the action of HCl on alcohol (II), instead of the chloride we obtained a tetrahydrofuran derivative, i.e. cyclization of the alcohol occurs under the influence of the acid medium, while the halogen derivative was only found in traces.

EXPERIMENTAL

1. Synthesis of Methylethylcyclopropylcarbinol

The carbinol was obtained by the action of ethylmagnesium bromide on acetyltrimethylene. The product had b.p. 138-144° and was oxidized by $KMnO_4$ in order to remove unsaturated impurities. Yield of alcohol with b.p. 141-143° was 54%. There was also obtained 8.6 g (about 5%) of a fraction with b.p. 70-72° at 17 mm and 170-172° at 760 mm, corresponding to the bromide with the constants:

n_D^{17} 1.4789; d_4^{17} 1.1763; MR_D 41.86. $C_7H_{13}Br\overline{|}$ Calculated: MR_D 41.83. Slabey's data [4]: n_4^{20} 1.4775; d_4^{20} 1.1873; b.p. 91-92° at 5 mm.

2. Interaction of Methylethylcyclopropylcarbinol with Formic Acid

150 g of the alcohol was heated to the boil while stirring for 1.5 hours with formic acid (1:2), i.e. approximately 38% (pH 0.88). After neutralization of the acid with dry sodium carbonate, extraction with ether and drying, the reaction products were fractionated in a column. The following fractions were isolated: 1st fraction, 102-107°, 29.4 g (23%); 2nd fraction, 107-112°, 6.5 g (5%); 3rd fraction, 119-122°, 14.5 g (9.6%); 4th fraction, 122-162°, 2.1 g (1.3%); 5th fraction, 162-167°, 57.0 g (30%). The residue in the flask, weighing 16.8 g, was fractionated in vacuum. Examination of first fraction with b.p. 102-107°. The fraction gave a reaction for the carbonyl group. A second fractionation in the column yielded a fraction with b.p. 104-106°. However, this fraction likewise gave traces of the 2,4-dinitrophenylhydrazone of acetyltrimethylene. For final purification, the compound was stood for several days over metallic Na and then refluxed with fresh Na for 3 hours on a funnel heater. A brown, gelatinous precipitate of the sodium derivative of the ketone separated. The liquid portion was drained and twice distilled over metallic Na. A second fractionation gave a fraction with b.p. 104-106°.

n_D^{15} 1.4430; d_4^{15} 0.7886; MR_D 32.27; $C_7H_{12}\overline{|}$ Calculated: MR_D 32.61; $C_7H_{12}\overline{|}_2$ Calculated: MR_D 33.69. Slabey's data [4] for the two isomeric cyclopropylbutenes: b.p.106.55°; n_D^{20} 1.4428; d_4^{20} 0.7810; b.p. 107.46°; n_D^{20} 1.4474; d_4^{20} 0.7874.

Oxidation of the hydrocarbon. Oxidation of 7.3 g hydrocarbon required 23.1 g $KMnO_4$. The MnO_2 was drained and washed with hot water. The neutral products were driven off from the solution. The first drops of distillate gave a copious precipitate with 2,4-dinitrophenylhydrazine; m.p. 145° (from alcohol); no depression with the 2,4-dinitrophenylhydrazone of acetyltrimethylene. From the acidified solution were distilled the volatile acids; formic acid was detected in the distillate (qualitative test with $HgCl_2$). The solution of volatile acids was heated on a boiling water bath with excess of freshly precipitated silver carbonate. The precipitate was filtered and water was removed from the filtrate in vacuum. Analysis of the silver salts showed acetic acid to be present.

0.0705 g sub.: 0.0456 g Ag. Found %: Ag 64.68. $C_2H_3O_2Ag$. Calculated %: Ag 64.67.

From the aqueous solution of the nonvolatile acids was isolated oxalic acid; after several sublimations it had m.p. 185° and did not give a depression with authentic oxalic acid. The results show that the hydrocarbon with b.p. 104-106° is a mixture of hydrocarbons with an open chain and a three-membered ring.

The second fraction with b.p. 107-112° was acetyltrimethylene (2,4-dinitrophenylhydrazone with m.p. 146°).

The third fraction with b.p. 118-122° corresponded to 2,2-methylethyltetrahydrofuran. It was given a preliminary purification from acetyltrimethylene by heating with Na and by distillation over fresh Na.

n_D^{20} 1.4230; d_4^{20} 0.8593; MR_D 33.86. $C_7H_{14}O$. Calculated: MR_D 33.94. The constants agreed completely with those previously obtained by us [1].

Fraction 5 with b.p. 162-167°. Analyses showed this fraction to be a mixture of the primary alcohol 3-methyl-3-hexen-6-ol and its formate.

d_4^{20} 0.8932; n_D^{20} 1.4398; $C_8H_{14}O_2$ (calculated on the ester) MR_D 41.88. $C_7H_{14}O$ (calculated on the alcohol) MR_D 33.62. $C_8H_{14}O_2$. Calculated: MR_D 40.34. $C_7H_{14}O$. Calculated: MR_D 35.58.

0.1008 g sub.: 0.2573 g CO_2; 0.0998 g H_2O. Found %: C 69.61; H 11.07. $C_7H_{14}O$. Calculated %: C 73.62; H 12.35. $C_8H_{14}O_2$. Calculated %: C 67.57; H 9.92.

Hydrolysis of the mixture of alcohol and ester. 20 g substance was heated to boiling with twice the amount of 10% potassium carbonate solution with stirring. Hydrolysis was carried out for 15 hours. The product was extracted with ether. After drying and driving off the solvent, a substance was obtained with b.p. 169-170°. Yield of alcohol 15 g.

d_4^{17} 0.8610; n_D^{17} 1.4510; MR_D 35.64. $C_7H_{14}O$. Calculated: MR_D 35.58. The constants agreed with our previous data [5].

0.1028 g sub.: 21.5 ml CH_4 (15.5°, 757 mm). OH number 0.988.

Oxidation of mixture of primary alcohol with its formic ester (b.p. 162-167°). Oxidation of 10 g substance consumed 37 g $KMnO_4$. The first drops of distillate of neutral products gave a precipitate with 2,4-dinitrophenylhydrazine with m.p. 116-117° (from alcohol). A mixed test with the 2,4-dinitrophenylhydrazone of authentic methylethyl ketone did not give a depression. Among the volatile acids was found formic acid. The non-volatile acids were extracted with ether in an extractor. After drying and driving off the ether, nearly the entire mass crystallized. The crystals were pressed on porous plate. Yield of acid 2 g; it was sublimed and recrystallized from benzene. M.p. 67°. No depression in test with authentic methylethylglycolic acid.

Action of $MgCH_3I$ on the mixture of primary alcohol and its ester. To the $MgCH_3I$ prepared from 3.5 g metallic Mg, 20.5 g CH_3I and 100 ml ether was added 12.5 g of the substance with m.p. 162-167° in 20 ml ether. The organo-Mg complex was decomposed with water and sulfuric acid (1:5). The reaction products were extracted with ether and dried with potassium carbonate. The ether extract was then divided into two parts. The first part, after driving off the ether, was distilled at normal pressure.

The first fraction, consisting of residues of ether and of formed isopropyl alcohol, came over at 40-115°, after which the temperature rose rapidly to 130° and then began to fall although material distilled over the whole time. The temperature fell to 120° and did not rise any higher. When the whole of the distillate was redistilled, it boiled at 120-122° and its constants corresponded to those of 2,2-methylethyltetrahydrofuran.

d_4^{20} 0.8603; n_D^{20} 1.4230 ; MR_D 33.74. $C_7H_{14}O$. Calculated: MR_D 33.94.

The second part, after removal of the ether, was distilled in vacuum to give a small fraction with b.p. up to 68° at 8 mm and a main fraction with b.p. 68-71° at 8 mm (n_D^{20} 1.4500), corresponding to 3-methyl-3-hexen-6-ol.

In a second experiment the organo-Mg complex was decomposed with water alone without addition of acid. The fractions so obtained were: 1) 50-160°; 2) 160-165° (a few drops); 3) 166-168°; yield 50.6%; n_D^{20} 1.4495.

Consequently, the isomerization of alcohol (II) to the tetrahydrofuran derivative requires traces of acid and heating to above 70°.

Examination of the high-boiling fractions. Repeated fractionations of the residue (16.8 g) in vacuum yielded a fraction with b.p. 112-114° at 14 mm. This was of the same order as the boiling point of the monoester of the glycol which we isolated after interaction of dimethylcyclopropylcarbinol with formic acid [2]. However, the analyses performed on the fraction with b.p. 112-114° at 14 mm showed that it was not a perfectly homogeneous substance although its boiling point did not change even after two more fractionations.

d_4^{16} 0.9667; n_D^{16} 1.4565; MR_D 45.01. $C_8H_{16}O_3$. Calculated: MR_D 42.45.

0.1065 g sub.: 0.2508 g CO_2; 0.1005 g H_2O. 0.1304 g sub.: 18.0 ml CH_4 (13.5°; 773 mm). Found %: C 64.20; H 10.5. OH number 0.9740. $C_8H_{16}O_3$. Calculated %: C 60.00; H 10.00; OH number 1.

Hydrolysis of substance with b.p. 112-114° at 10 mm. 4 g substance was heated with twice the amount of 20% potassium carbonate solution. The products of hydrolysis were extracted with ether. After drying and removal of the ether, the residue was distilled in vacuum to give 0.45 g viscous substance with b.p. 122-123° at 8 mm (n_D^{20} 1.4600). The aqueous solution was acidified with sulfuric acid and the volatile acids distilled with steam. Formic acid was detected in the distillate. The fraction with b.p. 122-123° at 8 mm is evidently methylethyltetramethylene glycol, but its minute amount prevented its further examination. For the purpose of identification the glycol was synthesized.

Synthesis of α-methyl-α-ethyltetramethylene glycol. To the ethyl magnesium bromide prepared from 12 g Mg and 54.5 g ethyl bromide was added 25.5 g acetopropyl alcohol dissolved in 50 ml ether. The organomagnesium complex was decomposed with water and NH_4Cl. The reaction products were extracted with ether. After drying, driving off the ether and distilling, a substance with b.p. 139-140° at 22 mm was obtained in a yield of 12 g (36%).

d_4^{20} 0.9713; n_D^{20} 1.4575; MR_D 37.62. $C_7H_{16}O_2$. Calculated: MR_D 37.82.

0.1331 g sub.: 0.3119 g CO_2; 0.1424 g H_2O. 0.0730 g sub.: 26.9 ml CH_4 (16°, 760 mm). Found %: C 63.90; H 11.97; OH number 2.066. $C_7H_{16}O_2$. Calculated %: C 63.63; H 12.12; OH number 2.

3. Interaction of 3-Methyl-3-hexen-6-ol with Hydrochloric Acid

6.3 g of the alcohol was stirred for 2 hours at room temperature with 24 ml hydrochloric acid in 1:1 dilution. The reaction product was extracted with ether and dried with potassium carbonate. Distillation gave two fractions: 1) 120-122°, 3.5 g (62%) and 2) 122-130°, 1.1 g. The first fraction is 2,2-methylethyltetrahydrofuran and the second is probably a mixture of the first fraction with traces of primary chloride since a Beilstein halogen test gave a positive result (b.p. of the chloride 154-156°).

4. Reaction of Methylethylcyclopropylcarbinol with Hydrochloric Acid

25 g of the alcohol was stirred at room temperature for 2 hours with 100 ml hydrochloric acid in 1:1 dilution. The upper layer was separated and dried with potassium carbonate. Fractionation gave 19 g of chloride with b.p. 154-156°, in agreement with our earlier data [3].

Ozonization of the chloride. 5 g chloride was ozonized in chloroform. After removal of the solvent, the ozonide was decomposed with water while heating on a water bath. The products of decomposition were extracted with ether; after drying and removing the solvent, a syrupy liquid remained, a portion of which was worked up with 2,4-dinitrophenylhydrazine solution to give an abundant yellow precipitate with m.p. 117° (from alcohol). A mixed melting point test with the 2,4-dinitrophenylhydrazone of methylethyl ketone did not give a depression. The remaining portion of the ozonization products was distilled in vacuum and gave a fraction with b.p. 102-105° at 23 mm which soon crystallized (m.p. 39°). The analysis corresponds to that of β-chloropropionic acid.

0.1066 g sub.: 0.1444 g AgCl. Found %: Cl 32.80. $C_3H_5O_2Cl$. Calculated %: Cl 32.71.

Ozonization did not yield any products other than methylethyl ketone and β-chloropropionic acid.

SUMMARY

1. The interaction of methylethylcyclopropylcarbinol with formic acid (pH 0.88) was studied.

2. It was established that this reaction proceeds in a similar manner to the reaction of formic acid with dimethylcyclopropylcarbinol; it differs from the latter, however, in that a mixture of hydrocarbons is also formed.

3. In addition to the hydrocarbons, the reaction gives 5 substances: a primary alcohol — 3-methyl-3-hexen-1-ol — and its formic ester; 2,2-methylethyltetrahydrofuran; α,α-methylethyltetramethylene glycol; and the partial formic ester of the glycol.

4. It was established that the product of reaction of methylethylcyclopropylcarbinol with hydrochloric acid is the unsaturated primary chloride, 3-methyl-6-chloro-3-hexene, whose structure was confirmed by ozonization.

5. It was established that the method of oxidation with $KMnO_4$ solution of compounds containing a secondary-tertiary double bond does not give accurate results.

6. The glycol, 3-methylhexane-3,6-diol ., was synthesized for the first time.

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* See Consultants Bureau English translation, page 891.

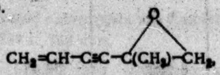
** See Consultants Bureau English translation, page 1553.

*** See Consultants Bureau English translation, page 437.

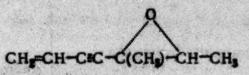
ADDITION OF AMMONIA AND DIETHYLAMINE TO OXIDES OF THE VINYLACETYLENE SERIES

F. Ya. Perveev and N. I. Kudryashova

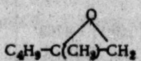
Numerous investigations have been devoted [1] to the addition of ammonia and amines to olefinic α-oxides; up to now, however, the addition of ammonia and amines to α-oxides of the vinylacetylenic series has not been studied. We considered it was necessary to study the influence of the vinylacetylene radical upon both the reactivity of oxides and the order of addition of ammonia. The compounds investigated were 2-methyl-oxido-1,2-hexen-5-yne-3 (I), 3-methyl-oxido-2,3-hepten-6-yne-4 (II) [2] and, for comparison, the saturated oxide, 2-methyl-oxido-1,2-hexane (III).



(I)



(II)



(III)

In the reaction of the oxides with ammonia, it was established that the velocity of addition of ammonia depends on the structural features of the oxides. For example, with oxide (I) at the ordinary temperature the reaction is completed in 8 hours. In these conditions oxide (II) reacted only to the extent of 50% in 8 days. The saturated oxide (III) practically does not react at room temperature. The reaction proceeds to completion only on heating in a sealed tube for 20-25 hours at 100°.

The addition of diethylamine to oxide (I) proceeds slowly more than that of ammonia (over a period of 46 hours, 1/3 of the original amount of oxide reacted). Addition of alkaline catalysts has practically no influence on the rate of addition of ammonia and diethylamine.

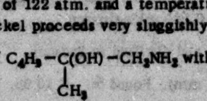
The following method was adopted for preparation of the aminoalcohols: To a 33% aqueous solution of ammonia (5-fold excess) with continuous stirring at room temperature was added the oxide. The duration of stirring was mentioned above. In the absence of intensive stirring, the unsaturated oxides react with ammonia to form resins, and hydroxyamines could not be isolated.

The physical constants of the prepared compounds are set forth in the table.

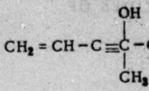
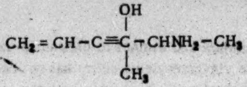
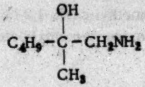
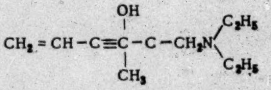
The prepared unsaturated hydroxyamines are liquids with an unpleasant odor, readily soluble in water, ether and alcohol; they polymerize even when kept in a sealed tube. 1-Amino-2-methyl-2-hydroxyhexene-5-yne-3 (I') crystallizes on keeping (m.p. 44.5-45.5°).

The prepared hydroxyamines are thermally unstable; they decompose completely when heated in a vacuum at above 140°; they do not form picrates.

1-Amino-2-methyl-2-hydroxy-hexen-5-yne-3 (I') is completely hydrogenated over Raney nickel in an autoclave at a pressure of 122 atm. and a temperature of 50-55°. At the ordinary temperature and pressure hydrogenation over Raney nickel proceeds very sluggishly.

Reaction of  $C_4H_9-\underset{\displaystyle CH_3}{\underset{|}{C}}(OH)-CH_2NH_2$ with α-naphthylisocyanate gives a crystalline product with m.p. 115-116° (a urea derivative). A mixed melting test of the urea derivatives prepared from the product of hydrogenation of the unsaturated hydroxyamine and the saturated aminoalcohol (III') did not give a depression.

The identity of the physical constants of the product of hydrogenation and those of 1-amino-2-methyl-hexanol-2 and the absence of a depression in the mixed melting test are evidence of the identity between the two substances. On this basis we may assume that the addition of ammonia to unsaturated oxides follows the K. A. Krasusky

Formula	B.p. (°C)	n_D^{20}	d_4^{20}	MR_D	
				Calculated	Found
I'.  $CH_2=CH-C\equiv C(OH)(CH_3)-C-CH_2NH_2$	91-92 (4 mm)	1,5165	1.0078	36.4	37.5
II'.  $CH_2=CH-C\equiv C(OH)(CH_3)-CHNH_2-CH_3$	97-98 (7 mm)	1.5061	0.9771	41,62	42,47
III'.  $C_4H_9-C(OH)(CH_3)-CH_2NH_2$	85-86 (7 mm)	1.4540	0.9045	39.47	39,29
IV. Product of complete hydrogenation of (I').	69-70 (3 mm)	1.4545	0.9095	39.47	39,11
V  $CH_2=CH-C\equiv C(OH)(CH_3)-C-CH_2N(C_2H_5)_2$	92-93 (7 mm)	1.4762	0.8915	55.99	57.36

rule [4] (the oxide ring is broken at the most hydrogenated atom of carbon)

The saturated oxide (III) was synthesized by the Grignard method by the action of chloroacetone on butylmagnesium bromide. The chloroacetone was added quickly to the reaction mixture in the course of a few minutes with cooling to −10 to −12°. Slow addition of the chloroacetone with less intensive cooling leads predominately to an alcohol with high molecular weight [3].

EXPERIMENTAL

Preparation of 1-Amino-2-methyl-2 hydroxyhexen 5-yne-3 (I')

200 ml 33% aqueous solution of ammonia was placed in a round-bottomed flask fitted with mechanical stirrer and mercury seal. Addition was then made of 25 g 2-methyl-oxido-1,2-hexen-5-yne-3 [2]. The reaction mixture was stirred for several hours at room temperature. The reaction was assumed to be at an end when the oxide had completely dissolved. The water and excess ammonia were taken off in vacuum and the residual dark-brown liquid dissolved in ether. The ethereal solution was dried with $MgSO_4$, the ether was removed, and the product distilled in vacuum. Yield 20 g hydroxyamine (69%).

0.2680, 0.2729 g substance: 24.6, 24.8 ml N_2 (16°, 766.8 mm). 0.1379, 0.1151 g substance: 58.1, 47.7 ml CH_4 (14.5°, 761.8 mm). Found %: N 10.8, 10.7 active H 1.739, 1.750. $C_7H_{11}ON$. Calculated %: N 11.19; active H 1.613

Hydrogenation. 9.5 g hydroxyamine was dissolved in methyl alcohol and hydrogenated over Raney nickel in a rotating autoclave (volume 350 ml) at 50-55° and an initial pressure of 122 atm. After 4 hours' hydrogenation the pressure had dropped to 91 atm., and it then remained constant for an hour. Hydrogen absorption was 10,850 ml. Hydrogenation of the double and triple bond requires 10,500 ml hydrogen

After driving off the methyl alcohol, the product was dried and distilled in vacuum.

0.1521, 0.1439 g substance: 14.25, 13.4 ml N_2 (18°, 761.8 mm). Found %: N 10.88, 10.83. $C_7H_{17}ON$. Calculated %: N 9.68.

With α-naphthylisocyanate in ligroine the substance forms a crystalline urea derivative. After recrystallization from benzene the white crystals had m.p. 115-116°.

0.1208, 0.1282 g substance: 10.0 ml N_2 (19°, 760 mm), 10.35 ml N_2 (18°, 763.3 mm). Found %: N 9.55, 9.40. $C_{18}H_{24}O_2N_2$. Calculated %: N 9.33.

Preparation of 2-Amino-3-methyl-3-hydroxyhepten-6-yne 4 (II')

The reaction was conducted as described above.

Reactants were 100 ml 33% aqueous ammonia and 10 g 3-methyl-oxido 2,3-hepten-6-yne-4. Stirring was continued for 8 days. Yield 5 g (43%) hydroxyamine.

0.1318, 0.1401 g substance: 11.8, 12.7 ml N_2 (18°, 747.1 mm). 0.1175 g substance: 41.8 ml CH_4 (16°, 747.1 mm). Found %: N 10.21, 10.33; active H 1.463. $C_8H_{13}ON$. Calculated %: N 10.06; active H 1.448.

Preparation of 2-Methyl-oxido-1,2-hexane (III)

To 0.75 mole butylmagnesium bromide in ethereal solution was added, with stirring and cooling, 60 g chloroacetone over a period of 9 hours. After decomposition with 30% acetic acid, the ethereal solution was separated and dried with $MgSO_4$; the ether was removed and the residue distilled in vacuum (5 mm) at 66-67°.

n_D^{15} 1.4500; d_4^{15} 1.0043. Found: MR_D 40.3. $C_7H_{15}OCl$. Calculated: MR_D 40.92.

0.2831, 0.2717 g substance: 0.2777, 0.2575 g AgCl. Found %: Cl 23.39, 23.45. $C_7H_{15}OCl$. Calculated %: Cl 23.53.

The prepared chlorohydrin was dissolved in ether and by treatment with pulverized KOH gave the oxide (III) with b.p. 135-136° at 762 mm.

n_D^{20} 1.4111; d_4^{20} 0.8304. Found MR_D 34.15. $C_7H_{14}O$. Calculated MR_D 33.97.

0.1018, 0.1032 g substance: 0.2742, 0.2775 g CO_2; 0.1146, 0.1149 g H_2O. Found %: C 73.51, 73.39; H 12.60, 12.45. $C_7H_{14}O$. Calculated %: C 73.63; H 12.36.

Preparation of 2-Methyl-2-butyl-2-hydroxyethylamine (III')

A mixture of 20 g of the saturated oxide (III) and 60 ml 33% aqueous ammonia in a sealed tube was heated at 100° for 20-25 hours. After driving off the excess of ammonia and water, 8 g aminoalcohol was isolated.

0.1350 g substance: 12.7 ml N_2 (17°, 759.3 mm). 0.1435 g substance: 54.4 ml CH_4 (15.5°, 757.8 mm). Found %: N 10.78; active H 1.585. $C_7H_{17}ON$. Calculated %: N 10.68; active H 1.536.

Reaction of α-naphthylisocyanate in ligroine with the hydroxyamine gave a urea derivative — a crystalline substance with m.p. 109-110° (from benzene).

Condensation of 2-Methyl-oxido-1,2-hexen-5-yne-3 (I) with Diethylamine

To an aqueous solution of 50 ml diethylamine was added 15 g oxide (I). The mixture was left for 46 hours at room temperature and shaken from time to time. 6 g unreacted oxide and 10 g tertiary aminoalcohol (V) were isolated. When the oxide was kept in contact with diethylamine for 96 hours, the yield of aminoalcohol increases to 85.8%.

0.1535 g substance: 20.6 ml CH_4 (15°, 767.3 mm). 0.2107 g substance: 13.2 ml N_2 (16°, 762.4 mm). Found %: active H 0.570; N 7.76. $C_{11}H_{19}ON$. Calculated %: active H 0.556; N 7.73.

SUMMARY

1. Reaction of the oxides 2-methyl-oxido-1,2-hexen-5-yne-3 and 3-methyl-oxido-2,3 hepten-6-yne-4 with ammonia gave the aminoalcohols: 1-amino-2-methyl-2-hydroxy-hexen-5-yne-3 and 2-amino-3-methyl 3-hydroxy-hepten-6-yne-4.

2. Reaction of 2-methyl oxido-1,2-hexen-5-yne-3 with diethylamine gave a tertiary aminoalcohol of the vinylacetylenic series.

3. It was established that the velocity of addition of ammonia in the given conditions depends on the structural characteristics of the oxides.

4. On the model of 1-amino-2-methyl-2-hydroxyhexen-5-yne 3 it was shown that ammonia adds on to oxides of the vinylacetylenic series according to the K. A. Krasusky rule.

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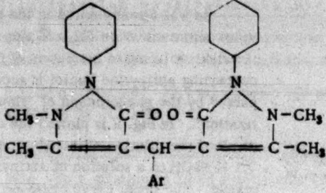
* See Consultants Bureau English translation, page 1623

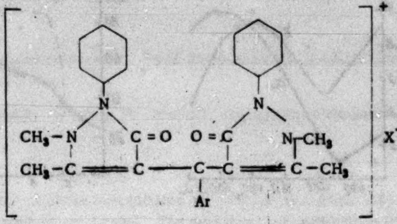
DYES CONTAINING ANTIPYRINE NUCLEI. III

O. F. Ginzburg

Interaction of antipyrine with benzaldehyde is known to give diantipyrylphenylmethane [1]. Experiments showed that also other aromatic aldehydes, such as o-, m-, and p-nitrobenzaldehydes, α-naphthaldehydes, p-chlorobenzaldehyde and vanillin, in aqueous or aqueous-alcoholic solutions in presence of hydrochloric acid react with antipyrine to form compounds of the diantipyrylarylmethane series (I). Like diantipyrylphenylmethane [2], these compounds are leuco bases of dyes (II), similar in structure and properties to the basic triphenylmethane dyes.

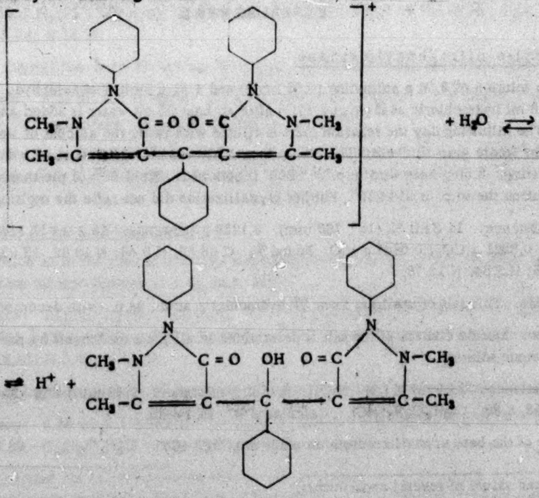


(I)



(II)

Dyes containing antipyrine nuclei are salts and resemble the basic triphenylmethane dyes [3] in undergoing hydrolysis in aqueous solutions; in the case of the dye known as antipyrine orange, to take an example, this hydrolysis may be represented by the following scheme:



(III)

A study of the acid-base equilibrium in aqueous solutions of dyes containing antipyrine nuclei enabled determination of their hydrolysis constants (K_h) and in turn of the dissociation constants (K_a) of the carbonyl compounds formed from these dyes. The data are set forth in Table 1.

TABLE 1

Name of compound	K_0*
Diantipyrylphenylcarbinol [3]	$2.88 \cdot 10^{-8}$
Diantipyryl-p-chlorophenylcarbinol	$1.05 \cdot 10^{-8}$
Diantipyryl-p-nitrophenylcarbinol	$3.17 \cdot 10^{-10}$

Examination of the tabulated data shows that the introduction into the phenyl group in the para-position to the central carbon atom of a nitro group or of a chlorine atom very considerably lowers the basicity of the carbinol and, consequently, increases the hydrolysis of the corresponding dye. It is also noteworthy that although the basicity of diantipyryl-p-chlorophenylcarbinol is higher than that of diantipyryl-p-nitrophenylcarbinol, the dye formed from the latter has a rather deeper color (Fig. 1, curve a) than the dye obtained from diantipyryl-p-chlorophenylcarbinol (Fig. 1, curve b). A study was also made of the hydrolysis of dyes containing antipyrine nuclei in 60% aqueous acetone.

The data set forth in Tables 2 and 3 show that hydrolysis of the dyes in 60% aqueous acetone is approximately 10 times greater than in water.

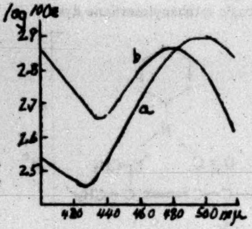


Fig. 1.

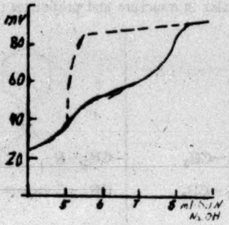


Fig. 2.

As was already noted in the previous communication [2], addition of caustic alkali solution to a solution of dyes containing antipyrine nuclei is accompanied by the phenomenon of "slow neutralization". In Fig. 2 is plotted the change of pH of the solution observed on adding 0.1 N NaOH to a solution of antipyrine orange. The upper curve characterizes the pH of the solution observed immediately after addition of each portion of alkali; the lower one shows the pH of the solution after 20 minutes. The change of pH of the solution, as follows from inspection of equation (III), is associated with the establishment of equilibrium in the solution.

EXPERIMENTAL

1. Diantipyryl-o-nitrophenylmethane

Base. To a solution of 3.76 g antipyrine (0.02 mole) and 1.51 g o-nitrobenzaldehyde (0.01 mole) in 15 ml alcohol is added 8 ml hydrochloric acid (sp gr.1.17). After an hour 25 ml water is added and the alcohol is driven off by heating. The following day the reaction mass is diluted with twice the amount of water. A precipitate rapidly forms and the whole mass thickens. The precipitate is filtered off and treated with dilute sodium carbonate solution while heating. 3.50 g base with m.p. 207-209° is obtained. Yield 69% of the theoretical. After two crystallizations from toluene the m.p. is 214-215°. Further crystallization did not raise the melting point.

0.1195 g substance: 14.3 ml N_2 (18°, 760 mm). 0.1259 g substance: 15.2 ml N_2 (18°, 759 mm). 0.1322 g substance: 0.3321 g CO_2; 0.0647 g H_2O. Found %: C 68.50; H 5.48; N 13.82, 13.93. $C_{29}H_{27}O_4N$. Calculated %: C 68.35; H 5.34; N 13.78.

Hydrochloride. This salt crystallizes from 3% hydrochloric acid. M.p. (with decomposition) 125-126°.

The hydrogen chloride content of the salt is determined in all the experiments by potentiometric titration of the aqueous acetone solution.

0.1470 g substance: 2.65 ml 0.1 N NaOH. 0.1531 g substance: 2.89 ml 0.1 N NaOH (T 0.00401). Found %: HCl 6.58, 6.89. $C_{29}H_{27}O_4N_5 \cdot HCl$. Calculated %: HCl 6.69.

The picrate of the base crystallizes from alcohol; m.p. 163-164°.

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* The data are mean values of several experiments.

0.0961 g substance: 12.6 ml N_2 (20°, 762 mm). 0.0997 g substance: 13.3 ml N_2 (20°, 760 mm). Found %: N 15.08, 15.54. $C_{29}H_{27}O_4N_5 \cdot C_6H_3O_7N_3$. Calculated %: N 15.17.

2. Diantipyryl-m-nitrophenylmethane*

The base is prepared by the same method as for diantipyryl-o-nitrophenylmethane. Yield 97% of the theoretical. After crystallization from toluene, m.p. 214°.

0.1380 g substance: 0.3468 g CO_2; 0.0663 g H_2O. 0.1290 g substance: 0.3228 g CO_2; 0.0623 g H_2O. 0.1265 g substance: 15.1 ml N_2 (20°, 758 mm). Found %: C 68.58, 68.29; H 5.38, 5.40; N 13.66. $C_{29}H_{27}O_4N_5$. Calculated %: C 68.35; H 5.34; N 13.78.

Hydrochloride. Crystallizes from 3% hydrochloric acid. M.p. with decomposition at 179-180°.

0.0977 g substance: 10.4 ml N_2 (23°, 755 mm). 0.9486 g substance: 0.2278 g AgCl. 0.3018 g substance: 5.21 ml NaOH (T 0.00404). Found %: N 12.20; Cl 5.95; HCl 6.38. $C_{29}H_{27}O_4N_5 \cdot 2H_2O \cdot HCl$. Calculated %: N 12.03; Cl 6.09; HCl 6.27.

Picrate of the base. M.p. 237° (from alcohol).

0.1311 g substance: 17.2 ml N_2 (16°, 751 mm). 0.1148 g substance: 15.3 ml N_2 (17°, 751 mm). Found %: N 15.11, 15.28. $C_{29}H_{27}O_4N_5 \cdot C_6H_3O_7N_3$. Calculated %: N 15.17.

3. Diantipyryl-α-naphthylmethane**

The procedure was the same as for diantipyryl-o-nitrophenylmethane. Yield 92.6% of the theoretical. After crystallization from toluene, alcohol or acetone, m.p. 254°.

0.1123 g substance: 10.7 ml N_2 (23°, 760 mm). Found: M 520.5; %: N 10.87. $C_{33}H_{30}O_2N_4$. Calculated M 514.5; %: N 10.88.

4. Diantipyryl-p-nitrophenylmethane

Base. To a solution of 10.28 g antipyrine (0.06 mole) in 20 ml concentrated hydrochloric acid (spgr. 118) is added a solution of 4.53 g p-nitrobenzaldehyde (0.03 mole) in 15 ml alcohol. The next day the precipitate is filtered, 30 ml water is added to the filtrate and the alcohol is driven off. An additional amount of salt comes down and is combined with the first portion. The salt is decomposed with dilute NaOH solution and 11.23 g base is obtained or 74.6% of the theoretical. M.p. 232° (from alcohol).

0.1163 g substance: 0.2921 g CO_2; 0.0568 g H_2O. 0.1300 g substance: 15.9 ml N_2 (21°, 752 mm). 0.1189 g substance: 14.5 ml N_2 (21°, 752 mm). Found %: C 68.51; H 5.47; N 13.76; 13.71. $C_{29}H_{27}O_4N_5$. Calculated %: C 68.35; H 5.34; N 13.78.

Hydrochloride. Crystallizes from 3% hydrochloric acid. Melts with decomposition at 218-221°.

0.1913 g substance: 3.42 ml 0.1 N NaOH. 0.2061 g substance: 3.71 ml 0.1 N NaOH (T 0.00408). Found %: HCl 6.66, 6.70. $C_{29}H_{27}O_4N_5 \cdot HCl$. Calculated %: HCl 6.69.

Picrate of the base. M.p. 248-249° (from alcohol). 0.1161 g substance: 15.4 ml N_2 (20°, 763 mm). 0.1211 g substance: 16.2 ml N_2 (20°, 762 mm). Found %: N 15.18, 15.38. $C_{29}H_{27}O_4N_5 \cdot C_6H_3O_7N_3$. Calculated %: N 15.17.

5. Diantipyryl-p-chlorophenylmethane

The base is prepared as in the case of diantipyryl-p-nitrophenylmethane. Yield 66.3% of the theoretical. After crystallization from toluene-ligroine (1 : 4), m.p. 169°.

0.1281 g substance: 12.6 ml N_2 (20°, 762 mm). 0.1139 g substance: 11.3 ml N_2 (20°, 762 mm). 0.1315 g substance: 0.3361 g CO_2; 0.0661 g H_2O. Found %: C 69.70; H 5.63; N 11.37, 11.47. $C_{29}H_{27}O_2N_4Cl$. Calculated %: C 69.81; H 5.46; N 11.24.

The hydrochloride crystallizes from 3% hydrochloric acid. M.p. with decomposition 201-203°.

0.1400 g substance: 2.50 ml 0.1 N NaOH. 0.1731 g substance: 3.08 ml 0.1 N NaOH (T 0.00408). Found %: HCl 6.83, 6.63. $C_{29}H_{27}O_2N_4Cl \cdot HCl$. Calculated %: HCl 6.82.

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* The preparation was carried out in collaboration with Z. Kh. Markazen.

** Preparation of diantipyryl-α-naphthylmethane and of the picrate of diantipyryl-α-naphthylcarbinol was carried out in collaboration with R. Ya. Selezneva.

Picrate of the base. M.p. 218-220° (from alcohol).

0,1095 g substance: 13.0 ml N_2 (23°, 765 mm). 0.1125 g substance: 13.1 ml N_2 (23°, 764 mm). Found %: N 13.65, 13.50. $C_{29}H_{27}O_2N_4Cl \cdot C_6H_3O_7N_3$. Calculated %: N 13.47.

6. Diantipyryl-m-methoxy-p-hydroxyphenylmethane

Base. To a solution of 3.76 g antipyrine (0.02 mole) in 15 ml hydrochloric acid (sp. gr. 1.18) is added 1.52 g (0.01 mole) vanillin. The latter dissolves quickly. After 30 minutes 15 ml water is added. The next day the precipitate is filtered off, and dissolved in 800 ml hot water. To the resultant solution is added 20 ml 20% sodium acetate solution. The white precipitate is filtered and dried. 4.85 g base is obtained or 95% of the theoretical. After two crystallizations from 50% alcohol, m.p. 146-148°.

0,1035 g substance: 9.9 ml N_2 (20°, 755 mm). 0.1112 g substance: 10.8 ml N_2 (20°, 756 mm). 0.1318 g substance: 0.3402 g CO_2; 0.0709 g H_2O. Found %: C 70.25; H 6.16; N 10.97, 11.15. $C_{30}H_{30}O_4N_4$. Calculated %: C 70.58; H 5.92; N 10.97.

Hydrochloride. It crystallizes from 2,5% hydrochloric acid. M.p. with decomposition 125-126°

0,2555 g substance: 4.70 ml 0.1 N NaOH (T 0.00400). 0,2649 g substance: 4.81 ml 0.1 N NaOH (T 0.00400) Found %: HCl 6.71, 6.67. $C_{30}H_{30}O_4N_4 \cdot HCl$. Calculated %: HCl 6.67.

Picrate. M.p. 208-209° (from alcohol).

0,1013 g substance: 11.8 ml N_2 (22°, 765 mm). 0,1216 g substance: 14.0 ml N_2 (21°, 765 mm). Found %: N 13.45, 13.33. $C_{30}H_{30}O_4N_4 \cdot C_6H_3O_7N_3$. Calculated %: N 13.31.

7. Oxidation of the Leuco Bases to Dyes

0,05 g leuco base is dissolved by heating in 1-2 ml 15% hydrochloric acid and to the boiling solution is added a few crystals of sodium nitrite. The solution acquires a deep-orange color. Formation of dyes is observed on oxidizing the following leuco bases: diantipyrylphenylmethane, diantipyryl-o-nitrophenylmethane, diantipyryl-m-nitrophenylmethane, diantipyryl-p-nitrophenylmethane, diantipyryl-p-chlorophenylmethane, diantipyryl-m-methoxy-p-hydroxyphenylmethane, and diantipyryl-α-naphthylmethane.

8. Diantipyryl-p-nitrophenylcarbinol

5 g diantipyryl-p-nitrophenylmethane hydrochloride is dissolved with heating in 50 ml concentrated hydrochloric acid. To the hot solution is added 0.5 g sodium nitrite in small portions over a period of 3-4 minutes, followed by 1.2 ml nitric acid (sp. gr. 1.4) dropwise over a period of 10 minutes. After addition of the whole of the nitric acid, the solution is boiled for 5-6 minutes and poured into 150 ml water. The orange solution is filtered and to the filtrate is added 15% NaOH solution until a precipitate appears. Dropwise addition is then made over a period of two hours of 2% NaOH solution until the reaction is alkaline to phenolphthalein. The next day the solution with precipitate is heated to the boil. After cooling, the precipitate is filtered and dried. Yield 2.95 g base. After crystallization from benzene-gasoline (1 : 5) the m.p. is 180-181°.

0.1077 g substance: 12.5 ml N_2 (25°, 768 mm). 0.1102 g substance: 12.9 ml N_2 (25°, 768 mm). 0.1201 g substance: 0,2923 g CO_2; 0.0579 g H_2O. Found %: C 66.37; H 5.40; N 13.36, 13.41. $C_{29}H_{27}O_4N_5$. Calculated %: C 66.24; H 5.17; N 13.31.

Picrate. M.p. 130-133° (from alcohol).

0.1121 g substance: 15.0 ml N_2 (21°, 752 mm). 0.1183 g substance: 15.9 ml N_2 (20°, 750 mm). Found %: N 15.23, 15.31. $C_{29}H_{27}O_4N_5 \cdot C_6H_3O_7N_3$. Calculated %: N 15.20.

9. Diantipyryl-p-chlorophenylcarbinol

The preparation is by the same procedure as for diantipyryl-p-nitrophenylcarbinol. Crystallizes from benzene-gasoline (1 : 5). M.p. 137-139°.

0.1239 g substance: 11.7 ml N_2 (20°, 759 mm). 0.1268 g substance: 12.1 ml N_2 (2[illegible]°, 7[illegible] mm). 0.1086 g substance: 0.2689 g CO_2; 0.0526 g H_2O. Found %: C 67.49; H 5.54; N 10.89, 10.[illegible]3. $C_{29}H_{27}O_3N_4Cl$. Calculated %: C 67.64; H 5.28; N 10.87.

10. Picrate of Diantipyryl-α-naphthylcarbinol

The oxidation of diantipyryl-α-naphthylmethane is performed in the same manner as that of diantipyryl-p-nitrophenylmethane. From 8 g diantipyryl-α-naphthylmethane is obtained 3.12 g crude base.

TABLE 2

Name of compound	Weight of sample (g)	0.1 N HCl (in ml)		pH of solution of equimolar mixture of dye and carbinol	K_h
		used in titration	required by calculation		
Diantipyryl-p-chlorophenylcarbinol	0.1049	2.02	2.04	6.10	$7.95 \cdot 10^{-7}$
Diantipyryl-p-nitrophenylcarbinol	0.1592	3.03	3.04	4.62	$2.40 \cdot 10^{-5}$

TABLE 3

Name of compound	Wt. of sample (in g)	0.1 N HCl solution (in ml)	pH of solution	K_h
Diantipyryl-p-chlorophenylcarbinol	0.0872	0.85	5.05	$8.92 \cdot 10^{-6}$
Diantipyryl-p-nitrophenylcarbinol	0.1612	1.54	3.70	$1.98 \cdot 10^{-4}$

To a hot solution of 2 g of the base in 60 ml alcohol is added 0.9 g picric acid in 20 ml alcohol. The next day the red crystals are filtered off, washed with a little alcohol and dried at 90-100°. Yield 1.9 g picrate with m.p. 235-236°. Further crystallizations did not change the melting point.

0.1040 g substance: 12.1 ml N_2 (21°, 756 mm). 0.1069 g substance: 12.4 ml N_2 (21°, 756 mm). Found %: N 13.33, 13.29. $C_{39}H_{31}O_9N_7$. Calculated %: N 13.22.

11. Study of Dissociation of the Carbonyl Compounds

a) A weighed amount of the carbinol is dissolved in a few ml 0.1 N hydrochloric acid and the solution made up to a volume of 200 ml. To the prepared solution of the dye is added 0.1 N NaOH solution in quantity sufficient for transformation of the dye into the carbinol compound. The solution gradually decolorizes. The obtained carbinol base remains in solution. After an hour the titration is performed. Readings are taken every 4-5 minutes after addition of each portion of hydrochloric acid. The titrated solution is at a temperature of 19°. The data are set forth in Table 2.

b) 0.1293 g diantipyryl-p-chlorophenylcarbinol is dissolved in 8.00 ml 0.1 N hydrochloric acid solution (T 0.00365) and the solution is mixed with 192 ml water. To the obtained hydrochloric acid solution of the dye is added 6.72 ml 0.1 N NaOH solution (T 0.00402). The pH of the solution is measured after 2 hours. The pH of the equimolar mixture of the dye and the carbinol is 6.15 (t 19°); K_0 1.11 · 10^{-8}.

c) A solution of 0.1761 g diantipyryl-p-nitrophenylcarbinol in 6.10 ml 0.1 N hydrochloric acid (T 0.00365) is mixed with 194 ml water. The solution is potentiometrically titrated. Temperature of solution, 19°. Readings are taken on the average every 4-5 minutes after addition of the particular portion of NaOH solution. With progressive addition of NaOH solution the solution loses color and by the end of the titration it is colorless. The formed diantipyryl-p-nitrophenylcarbinol remains in solution. Formation of diantipyryl-p-nitrophenylcarbinol required 3.36 ml 0.1 N NaOH (T 0.00402). The calculated amount of NaOH solution with T 0.00402 is 3.34 ml; the pH of the equimolar mixture of dye and carbinol is 4.60. Dissociation constant at K_0 3.16 · 10^{-10}.

d) A weighed amount of carbinol is dissolved in 70 ml 60% aqueous acetone. To the obtained solution is added 0.5 equivalent of 0.1 N hydrochloric acid solution (T 0.00365). The pH of the solution is measured after 2 hours (t 19°). The data are set forth in Table 3.

SUMMARY

1. Diantipyryl-o-nitrophenylmethane, diantipyryl-m-nitrophenylmethane, diantipyryl-p-nitrophenylmethane, diantipyryl-p-chlorophenylmethane, diantipyryl-α-naphthylmethane and diantipyryl-m-methoxy-p-hydroxyphenylmethane are leuco compounds of the corresponding dyes.

2. Introduction of a nitro group or chlorine into the molecule of diantipyryl-phenylcarbinol in the para-position to the central carbon atom lowers the dissociation of the hydroxyl group.

3. Hydrolysis of dyes containing antipyrine nuclei in 60% aqueous acetone is approximately 10 times as great as in water.

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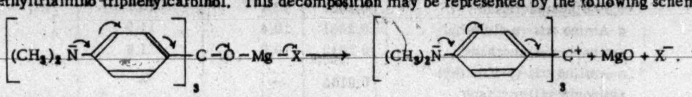
* See Consultants Bureau English translation, page 1575.

INTERACTION OF AMINOTRIARYLCARBINOLS WITH ORGANOMAGNESIUM COMPOUNDS

O. F. Ginzburg

It is known that magnesium alcoholates in the majority of cases do not undergo further transformations under the influence of organomagnesium compounds and the literature only mentions a few cases of reaction between magnesium alcoholates and organomagnesium compounds, leading ultimately to substitution of the alcoholate group OMgX by a hydrocarbon radical [1]. Bearing in mind that in aminotriphenylcarbinols the mobility of the hydroxyl groups is especially great and many times greater than the mobility of the hydroxyl groups in alcohols, it might be expected that also the O-magnesium derivatives of aminotriphenylcarbinols will readily decompose with rupture of the carbon-oxygen bond. Experiments confirmed this supposition. Thus, for example, on mixing phenetole solutions of 4,4',4"-hexamethyltriamino-triphenylcarbinol and methylmagnesium iodide, apart from evolution of methane, the formation is observed of a dye which partly remains in solution and imparts to the latter an intense color. Formation of a dye shows that decomposition occurs in the reaction mass of the magnesium derivative of 4,4',4"-hexamethyltriamino-triphenylcarbinol. This decomposition may be represented by the following scheme:



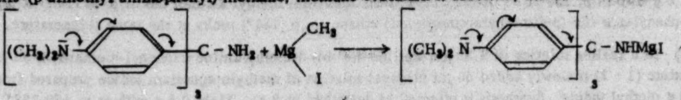
Similar results were obtained in a study of the reaction of 4,4'-tetramethyl-diamino-triphenylcarbinol, 9-phenyl-9-hydroxy-10-methyl-9,10-dihydroacridine, and diantipyryl-phenylcarbinol with methylmagnesium iodide.

As already shown by Freund and Beck [2], crystal violet enters into reaction with organomagnesium compounds with formation of derivatives of tetrasubstituted methane. Consequently, if 4,4',4"-hexamethyltriamino-triphenylcarbinol is treated with a few equivalents of methylmagnesium iodide, the initially formed dye enters into further reaction with the methylmagnesium iodide to give *a,a,a*-tris-(p-dimethylaminophenyl)-ethane.

Similarly, the reaction of 4,4'-tetramethyldiamino-triphenylcarbinol with methylmagnesium iodide gave *a*-phenyl-*a,a*-bis-(p-dimethylaminophenyl)-ethane. The preparation of *a,a,a*-tris-(p-dimethylaminophenyl)-ethane and of *a*-phenyl-*a,a*-bis-(p-dimethylaminophenyl)-ethane was performed by adding a solution of methylmagnesium iodide in ether to a benzene-ether solution of the respective aminotriphenylcarbinol. In this reaction it was noted that formation of the dye is hindered if the methylmagnesium iodide is added to the benzene-ethereal solutions of the aminotriphenylcarbinols in large portions. This is because organomagnesium compounds are capable of adding on to the amino groups of aminotriphenylcarbinols, thereby eliminating the influence of the amino groups on the polarization of the linkage between the methane carbon atom and the oxygen atom, and so hindering the rupture of this linkage.

It should be mentioned that neither *a*-phenyl-*a,a*-bis-(p-dimethylaminophenyl)-ethane nor *a,a,a*-tris-(p-dimethylaminophenyl)-ethane could be converted into a dye with the help of lead peroxide.

Further experiments showed that formation of dyes also occurs on interaction of organomagnesium compounds with amino bases of triphenylmethane dyes. To mention one example, in the action of methylmagnesium iodide on *a*-amino-tris-(p-dimethyl-aminophenyl)-methane, methane evolution is observed, due to the reaction



and there is also obtained crystal violet which, in presence of methylmagnesium iodide in the reaction mass, enters into reaction with the latter with formation of the above-mentioned α,α,α-tris-(p-dimethylaminophenyl)-ethane. But when methylmagnesium iodide acts on α-anilino-4,4'-bisdimethylaminotriphenylmethane at room temperature, as would be anticipated, no methane evolution is observed but malachite green is formed. The latter gradually enters into reaction with methylmagnesium iodide to form the above-noted α-phenyl-α,α-bis-(dimethylaminophenyl)-ethane.

Consequently, organomagnesium compounds, like strong acids, decompose amino bases and convert them into dyes.

EXPERIMENTAL

1. Determination of active hydrogen was carried out by the Chugaev-Tserevitinov method in phenetole solution at room temperature. The data obtained are set forth in the table.

No. of preparation	Name of substance	Wt. (g)	CH_4 (0°, 760 mm) (in ml)		Color of reaction mass
			evolved in 20 min.	calculated	
1	4,4'-Tetramethyldiamino-triphenylcarbinol	0.1963	12.2	12.7	Green
		0.2010	12.1	13.0	
2	4,4',4"-Hexamethyltri-aminotriphenylcarbinol	0.2142	10.4	12.3	Violet
		0.2149	10.6	12.4	
3	Diantipyryl-phenylcarbinol	0.2561	11.3	12.0	Orange
		0.2137	9.2	10.0	
4	9-Phenyl-9-hydroxy-10-methyl-9,10-dihydroacridine	0.2653	18.0	20.6	Light-brown
		0.2581	17.4	20.2	
5	α-Amino-tris-(p-dimethyl-aminophenyl)-methane	0.2061	10.4	11.9	Violet
		0.2012	10.0	11.6	
6	α-Anilino-tris-(p-dimethyl-aminophenyl)-methane	0.2185	–	–	Violet
7	α-Anilino-4,4'-bis-dimethyl-aminotriphenylmethane	0.1913	–	–	Green

2. α-Anilino-tris-(p-dimethylaminophenyl)-methane. A mixture of 0.50 g of the methyl ether of 4,4',4"-hexamethyltriaminotriphenylcarbinol (m.p. 158°) and 0.60 g aniline is heated for 2 hours at 135-145°. The melt is cooled and dissolved in 15 ml ether and the solution cooled to 0°. A white crystalline precipitate soon appears and is filtered, well washed with ether and dried. Yield 0.30 g of substance with m.p. 189-190°.

0.1132 g substance: 11.8 ml N_2 (20°, 767); 0.1167 g substance: 12.2 ml N_2 (20°, 768). Found %: N 12.14, 12.19. $C_{31}H_{36}N_4$. Calculated %: N 12.05.

3. α-Phenyl-α,α-bis-(p-dimethylaminophenyl)-ethane. a) To a boiling solution of 2.42 g 4,4'-tetramethyldiamino-triphenylcarbinol in 60 ml ether-toluene (1 : 2) is slowly added from a dropping funnel, with stirring, an ethereal solution of methylmagnesium iodide prepared from 0.85 g Mg and 4.96 g methyl iodide. The first 10 ml of solution is run in in the course of 30 minutes. After standing for an hour, further addition of the ethereal solution of methylmagnesium iodide is effected dropwise at the rate of 20 ml solution in 2 hours. After again standing for an hour, the remaining 20 ml solution is introduced dropwise in the course of 40 minutes. The reaction mass is then stirred and heated for 12 hours. After decomposition of the reaction mass with ice, the ether-toluene solution is separated from the aqueous layer. The aqueous layer and also the obtained precipitate are treated twice with small portions of ether which are then added to the main ether-toluene solution. The latter is then treated with three portions of 100 ml each of 1% hydrochloric acid. To the resultant aqueous extracts is added a saturated solution of sodium acetate; the precipitate that forms is filtered after 4 hours, washed with water and dried at 80°. Yield 1.0 g with m.p. 128-131°. After 2 crystallizations from methyl alcohol the m.p. is 134°. A mixed sample with α-phenyl-α,α-bis-(p-dimethylaminophenyl)-ethane (m.p. 134°) melts at the same temperature.

b) To a boiling solution of 2.39 g α-anilino-4,4'-bis-dimethylamino-triphenyl-methane in 60 ml ether-toluene mixture (1 : 2) is slowly added 50 ml ethereal solution of methylmagnesium iodide prepared from 0.64 g Mg and 3.8 g methyl iodide. Synthesis is effected as described in 3 a). Yield 0.6 g with m.p. 132-133°. After crystallization from alcohol the m.p. is 134°. A mixture of the prepared compound with α-phenyl-α,α-bis-(p-dimethylaminophenyl)-ethane (m.p. 134°) melts at the same temperature.

4. α,α,α-Tris-(p-dimethylaminophenyl)-ethane. To a boiling solution of 1.56 g 4,4',4"-hexamethyltriamino-triphenylcarbinol in 60 ml ether-toluene mixture (1 : 2) is slowly added 50 ml of an ethereal solution of the methylmagnesium iodide prepared from 0.59 Mg and 3,41 g methyl iodide. The synthesis is performed as described in 3 a). Yield 0,72 g substance with m.p. 201°. After crystallization from methyl alcohol the m.p. is 209-210°. Mixed test with α,α,α-tris-(p-dimethylaminophenyl)-ethane (m.p. 209-210°) gave the same melting point.

SUMMARY

In the interaction of aminotriarylcarbinols with organomagnesium compounds, apart from hydrocarbons, dyes are formed. The latter are also prepared by the action of organomagnesium compounds on the amino bases of triphenylmethane dyes.

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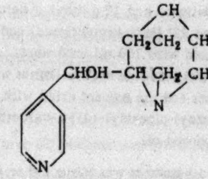
SYNTHESIS OF [5-ETHYLQUINUCLIDYL-(2)]-[PYRIDYL-(2)]-CARBINOL. V

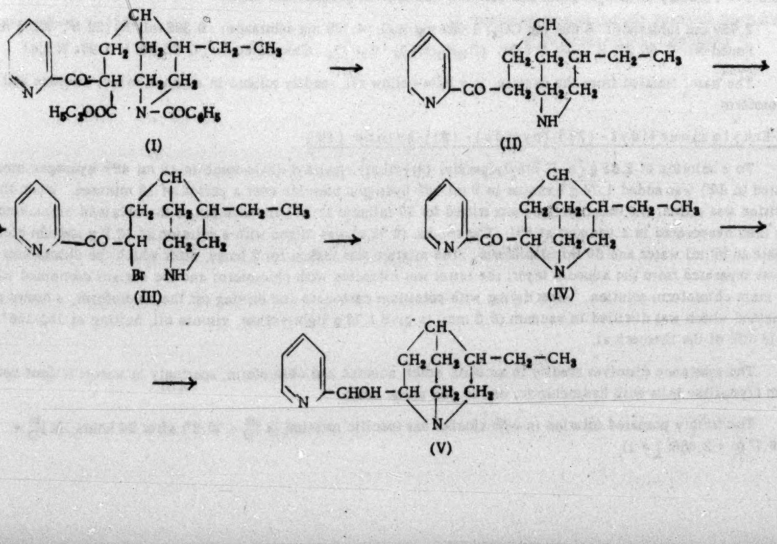
M. V. Rubtsov and V. A. Volskova

Comparison of hydroquinine with its pyridine analog containing a quinuclidine ring in the 4-position of the pyridine nucleus [1]



enabled us to establish that replacement of the quinoline nucleus in hydroquinine by a pyridine nucleus has relatively little effect on the chemotherapeutic activity of the preparation. It was interesting to ascertain the effect on the activity of the pyridine analog of hydroquinine of transfer of the ethylquinuclydyl-hydroxymethyl group from the 4-position to the 2-position of the pyridine nucleus.

For this purpose we synthesized [5-ethylquinuclidyl-(2)]-[pyridyl-(2)]-carbinol, starting from ethyl picolinate and ethyl benzoylhomocincholoiponate. Condensation of these esters gave the ketoester (I) which was converted by acid saponification into {β-[3-ethylpiperidyl-(4)]-ethyl} -[pyridyl-(2)]-ketone (II).



(I) (II) (III) (IV) (V)

Preparation of [5-ethylquinuclidyl-(2)]-[pyridyl-(2)]-ketone (IV) was carried out by the usual method via the corresponding C-bromo derivative (III).

Ethylquinuclidyl-pyridyl ketone (IV) is a light-yellow oil which distils in vacuum without decomposition; it exhibits the phenomenon of mutarotation. The carbonyl group of this compound is readily reduced to carbinol by hydrogenation of the dihydrochloride in an aqueous medium in presence of palladium black. The resultant mixture of stereoisomeric carbinols (V) is isolated in the form of a viscous oil which distilled in vacuum and, like hydroquinine, is transformed into the corresponding toxine (II) by boiling with dilute acetic acid.

Attempts to resolve the stereoisomeric carbinols with the help of d-tartaric or d-camphorsulfonic acid were unsuccessful; the mixture of stereoisomers was therefore subjected to chemotherapeutic examination and found to be inactive in avian malaria.

The tests were carried out on siskins infected with Plasmodium relictum.

EXPERIMENTAL

{β-[3-Ethylpiperidyl-(4)]-ethyl}-[pyridyl-(2)]-ketone (II)

To sodium ethylate, prepared from 2.4 g metallic sodium powder and 4.8 g absolute alcohol, in an ethereal medium was added with stirring 15 g ethyl picolinate and 17 g ethyl N-benzoylhomocincholoiponate. The ether was removed by heating the reaction mixture to 80° (bath temperature) and the mass was stirred at this temperature for 4 hours. On cooling, the mass was mixed with 150 ml iced water. The unreacted starting materials were extracted with ether and the aqueous solution was made neutral to litmus with the help of 10% sulfuric acid. The oil which separated out was extracted with ether and the extract dried with anhydrous sodium sulfate. After driving off the ether, 12.47 g (55.1%) {β-[3-ethyl-N-benzoyl-piperidyl-(4)]-α-carbethoxyethyl}-[pyridyl-(2)]-ketone (ketoester) was obtained in the form of a viscous dark-red oil.

Without further purification, the obtained ketoester was subjected to ketonic cleavage by boiling for 4 hours with ten times the quantity of 17% hydrochloric acid. After cooling, the solution was washed with ether several times to remove benzoic acid and then made alkaline with excess of 50% potassium hydroxide. The resultant oil was extracted with ether and the extract dried with potassium carbonate. Removal of the ether left 5.88 g {β-[3-ethylpiperidyl-(4)]-ethyl}-[pyridyl-(2)]-ketone in the form of a viscous dark-yellow oil. For the purpose of purification the ketone was dissolved in 10 ml absolute alcohol, 1.05 g anhydrous oxalic acid in 5 ml absolute alcohol was added and the solution was diluted with 125 ml dry acetone. After a few minutes a copious crystalline precipitate had formed. After standing overnight, the precipitate was filtered, washed with acetone and ether and recrystallized from a small quantity of alcohol. Yield 3.92 g (44.6%). A white crystalline powder with m.p. 175.5-177°; readily soluble in water and alcohol, insoluble in acetone and ether.

2.739 mg substance: 6.626 mg CO_2; 1.950 mg H_2O. 4.709 mg substance: 0.398 ml N_2 (22.5°, 726.5 mm).
Found %: C 65.97; H 7.96; N 9.34. $(C_{15}H_{22}ON_2)_2 \cdot C_2H_2O_4$. Calculated %: C 65.94; H 7.96; N 9.61.

The base, isolated from the oxalate, is a light-yellow oil, readily soluble in alcohol, ether, acetone and chloroform.

[5-Ethylquinuclidyl-(2)]-[pyridyl-(2)]-ketone (IV)

To a solution of 2.69 g {β-[3-ethylpiperidyl-(4)]-ethyl}-[pyridyl-(2)]-ketone in 19 ml 48% hydrogen bromide, heated to 60°, was added 1.74 g bromine in 9 ml 48% hydrogen bromide over a period of 15 minutes. When the addition was ended, the reaction mass was stirred for 20 minutes at 80°; the solution of the obtained bromoketone was then evaporated in a vacuum at 55°. The residue (6.72 g) was mixed with a solution of 12.2 g sodium bicarbonate in 60 ml water and 60 ml chloroform. The mixture was shaken for 2 hours, after which the chloroform layer was separated from the aqueous layer; the latter was extracted with chloroform and the extract combined with the main chloroform solution. After drying with potassium carbonate and driving off the chloroform, a brown oil remained which was distilled in vacuum (0.3 mm) to give 1.73 g light-yellow, viscous oil, boiling at 155-156°. Yield 65% of the theoretical.

The substance dissolves readily in alcohol, ether, acetone and chloroform, sparingly in water; it does not form crystalline salts with hydrochloric, oxalic and picric acids.

The freshly prepared solution in 96% alcohol has specific rotation $[\alpha]_D^{20}$ + 75.2°; after 24 hours, $[\alpha]_D^{20}$ + + 76.7° (c = 2.086; l = 1).

3.676 mg substance: 9.916 mg CO_2; 2.750 mg H_2O. 3.487 mg substance: 0.375 ml N_2 (31.5°, 728.5 mm). Found %: C 73.56; H 8.37; N 11.54. $C_{15}H_{20}ON_2$. Calculated %: C 73.72; H 8.25; N 11.47.

[5-Ethylquinuclidyl-(2)]-[pyridyl-(2)]-carbinol (V)

To a solution of 2.47 g [5-ethylquinuclidyl-(2)]-[pyridyl-(2)]-ketone in 20.2 ml 1 N hydrochloric acid was added 10 ml 2% palladium chloride solution. The mixture was shaken until the separated orange precipitate had dissolved; the solution was then hydrogenated at room temperature under a pressure of 40-60 mm water column. After the hydrogenation, the solution was filtered from catalyst and acidified with 40 ml 50% KOH. The base was extracted with ether and the extract dried with potassium carbonate. After driving off the ether, the residue was distilled in vacuum to give 2.38 g viscous oil which consisted of a mixture of the optical isomers of ethylquinuclidyl-pyridyl-carbinol. B.p. 139-143° at 0.3 mm. The oil had good solubility in alcohol, ether, chloroform; poor in water.

$[\alpha]_D^{20}$ + 70.8° in 96% alcohol (α 1.48; c 2.088; $\underline{l}$ = 1).

4.717 mg substance: 12.654 mg CO_2; 3.855 mg H_2O. 5.559 mg substance: 0.579 ml N_2 (24.5°, 723 mm). Found %: C 73.16; H 9.15; N 11.37. $C_{15}H_{22}ON_2$. Calculated %: C 73.12; H 9.01; N 11.37.

The prepared mixture must contain four stereoisomeric carbinols. Attempts to effect their resolution with the help of d-tartaric or d-camphorsulfonic acid proved unsuccessful. Boiling with dilute acetic acid leads to cleavage of the quinuclidine ring, this behavior being characteristic of the quinine alkaloids; in this case it led to formation of {β-[3-ethylpiperidyl-(4)]-ethyl}-[pyridyl (2)]-ketone.

SUMMARY

1. [5-Ethylquinuclidyl-(2)]-[pyridyl-(2)]-ketone was synthesized.

2. Catalytic hydrogenation of the ketone gives a mixture of the optical isomers of the corresponding carbinol which, on boiling with dilute acetic acid, undergoes like compounds of the quinine series, the reaction of "hydramino cleavage," and is transformed into {β-[3-ethylpiperidyl-(4)]-ethyl}-[pyridyl-(2)]-ketone.

3. The mixture of optical isomers of [5-ethylquinuclidyl-(2)]-[pyridyl-(2)]-carbinol proved to be inactive in tests on siskins infected with Plasmodium relictum.

LITERATURE CITED

[1] M. V. Rubtsov, J. Gen. Chem., 13, 702 (1943).

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of Pharmaceutical Chemistry

4.022 mg substance: [illegible] mg CO₂, [illegible] mg H₂O. [illegible] mg substance: [illegible] ml N₂ ([illegible]°, [illegible] mm). Found %: C [illegible]; H [illegible]; N [illegible]. [illegible]. Calculated %: C [illegible]; H [illegible]; N [illegible].

[illegible]-quinolinyl-[illegible]-[illegible]

A solution of [illegible] g [illegible] in [illegible] was hydrogenated [illegible] in [illegible] of [illegible] acid [illegible]. The [illegible] was [illegible] the [illegible], the solution was [illegible] under a pressure of [illegible]. [illegible] the hydrogenation, the solution was filtered from the catalyst and neutralized with [illegible] KOH. The base was extracted with ether and the [illegible] dried with potassium carbonate. After distilling off the ether, the residue was distilled in vacuum to give [illegible] g [illegible] of a mixture of the optical isomers of [illegible] piperidyl carbinol, b.p. [illegible] at 0.3 mm. The oil has good solubility in alcohol, ether, chloroform; poor in water.

$[\alpha]_D^{20}$ + 10.8° in 96% alcohol (c 1.[illegible]; l 0.5 dm) [illegible]

4.714 mg substance: 12.864 mg CO₂, [illegible] mg H₂O. [illegible] mg substance: [illegible] ml N₂ ([illegible]°, [illegible] mm). Found %: C [illegible]; H [illegible]; N [illegible]. [illegible]. Calculated %: C [illegible]; H [illegible]; N [illegible].

The prepared mixture of the isomers [illegible]. Attempts [illegible] with the [illegible] of a [illegible] the [illegible] with [illegible] in the [illegible] ring, this behavior [illegible] of the [illegible] of [illegible]-(4)-ethyl-[illegible] piperidyl-[illegible]-carbinol.

SUMMARY

1. [illegible]-quinolinyl-(4)-[illegible]-pyridyl-(2)-ketone was synthesized.

2. Catalytic hydrogenation of the ketone gives a mixture of the optical isomers of the corresponding carbinol, which, on boiling with [illegible] of the quinoline ring, [illegible] and is transformed into [illegible] ethylpiperidyl [illegible].

3. The mixture of optical isomers of [illegible] piperidyl-(2)-carbinol proved to be inactive in tests [illegible] with [illegible].

LITERATURE CITED

[1] A. V. [illegible] J. Gen. Chem. [illegible] (194[illegible]).

Received June [illegible], 194[illegible]

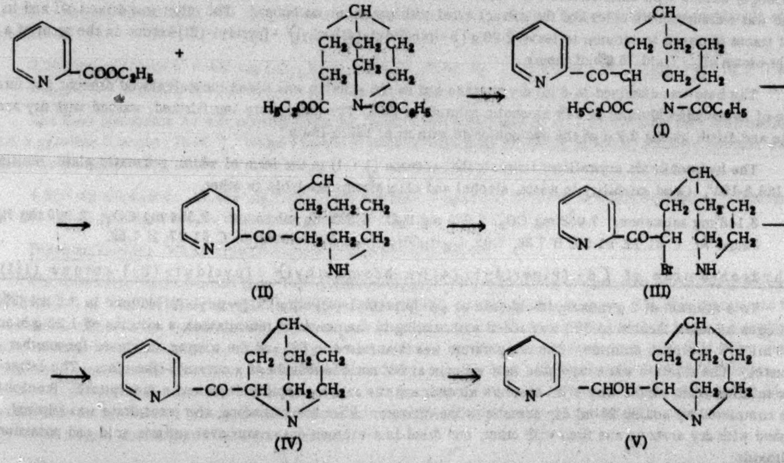
[illegible] Institute [illegible]

SYNTHESIS OF [QUINUCLIDYL-(2)]-[PYRIDYL-(2)]-CARBINOL. VI

M. V. Rubtsov and V. A. Volskova

In our previous papers we described analogs of hydroquinine containing the ethylquinuclidyl-carbonyl group in the 4- and 2-positions of the pyridine ring [1].

With the aim of further studying compounds of this series, we have synthesized [quinuclidyl-(2)]-[pyridyl-(2)]-carbinol. This compound was prepared from ethyl picolinate and ethyl β-[N-benzoylpiperidyl-(4)]-propionate.



The ketoester (I), prepared by condensation of the starting esters, was saponified with hydrochloric acid to {β-[piperidyl-(4)]-ethyl}-[pyridyl-(2)]-ketone (II), which was isolated in the form of the monohydrochloride melting at 182.5-184.5°. Treatment of the piperidylethyl-pyridyl-ketone with bromine in 48% hydrobromic acid gave the dihydrobromide of the corresponding C-bromoketone (III), a yellow crystalline powder with m.p. 170-171°. By treatment with bicarbonate solution, the bromoketone (III) was transformed into quinuclidyl-pyridyl-ketone (IV), which was obtained in the form of white prisms with m.p. 71.5-73°. Reduction of ketone (IV) to carbinol (V) was performed by hydrogenation of the dihydrochloride of the ketone in an aqueous medium in presence of palladium black. A mixture of the diastereoisomeric racemates was obtained in this way and was resolved by taking advantage of the differing solubility of their hydrochlorides in alcohol. The properties of the racemates are set forth in the table.

In tests on siskins infected with Plasmodium relictum, both racemates proved to be inactive.

EXPERIMENTAL

{β-[Piperidyl-(4)]-ethyl}-[pyridyl-(2)]-ketone (II)

To the sodium ethylate prepared from 1.25 g pulverized metallic sodium and 2.5 g absolute alcohol in a medium of absolute ether was added 7.5 g ethylpicolinate and 8.5 g ethyl β-[N-benzoyl-piperidyl-(4)]-propionate.

Designation of racemates	Base	Hydrochloride	Characteristic features
A	White clusters of needles, m.p. 118-119°	White microscopic prisms, m.p. 232-233°	Hydrochloride poorly soluble in cold alcohol
B	Small white prisms, m.p. 80-82°	White crystalline powder, m.p. 175-177°	Hydrochloride highly soluble in alcohol

The mixture was gradually heated on an oil bath to 80°; at the same time the ether was driven off. The mass was stirred for 4 hours at 80°, after which 50 ml benzene was added. The mixture was cooled to room temperature and shaken with 75 ml iced water. The aqueous layer was separated from the benzene layer, washed with ether, and treated with 10% sulfuric acid solution until neutral to litmus. The separated oil was extracted with ether and the extract dried with potassium carbonate. The ether was driven off to leave 5.91 g (57.6%) of {β-[N-benzoyl-piperidyl-(4)]-α-carbethoxyethyl}-[pyridyl-(2)]-ketone (ketoester).

The obtained ketoester was subjected to ketonic cleavage by boiling for 4 hours with ten times the quantity of 17% hydrochloric acid. After cooling, the solution was treated with 20% KOH until the reaction was weakly acid to Congo, washed with ether to remove benzoic acid and made alkaline with excess of 50% KOH. The separated base was extracted with ether and the extract dried with potassium carbonate. The ether was driven off and its last traces removed in vacuum to leave 2.23 g {β-[piperidyl-(4)]-ethyl}-[pyridyl-(2)]-ketone in the form of a light-brown oil. Yield 75.6% of theory.

The base was dissolved in 8 ml dry acetone and to the solution was added the calculated amount (for formation of monohydrochloride) of 14% alcoholic solution of HCl. The precipitate was filtered, washed with dry acetone and dried, giving 2.2 g of the hydrochloride with m.p. 182.5-184.5°.

The hydrochloride crystallizes from alcohol-acetone (1 : 1) in the form of white, prismatic plates melting at 189.5-190°. Good solubility in water, alcohol and chloroform; insoluble in ether.

3.146 mg substance: 7.058 mg CO_2; 2.070 mg H_2O. 4.302 mg substance: 9.654 mg CO_2; 2.990 mg H_2O. Found %: C 61.18, 61.20; H 7.36, 7.68. $C_{13}H_{18}ON_2 \cdot HCl$. Calculated %: C 61.27; H 7.52.

Dihydrobromide of {β-[Piperidyl-(4)]-α-bromoethyl}-[pyridyl-(2)]-ketone (III)

To a solution of 2 g monohydrochloride of {β-[piperidyl-(4)]-ethyl}-[pyridyl-(2)]-ketone in 7.5 ml 48% hydrogen bromide, heated to 50°, was added with stirring in the course of ten minutes, a solution of 1.25 g bromine in 9 ml 48% hydrogen bromide. The temperature was then raised to 80° and the stirring continued for another 15 minutes. The solution was evaporated in a vacuum at 55° until formation of a caramel-like mass. The latter went into solution when mixed with 1 ml absolute alcohol and the solution rapidly deposited a precipitate. Precipitation was completed by adding 25 ml dry acetone to the mixture. After brief standing, the precipitate was filtered, washed with dry acetone and then with ether, and dried in a vacuum-desiccator over sulfuric acid and potassium hydroxide.

A yellow, crystalline powder, m.p. 170-171° (with decomposition). Good solubility in water and alcohol, insoluble in acetone. Yield 3.08 g (84.6%).

0.1275 g substance: 0.1555 AgBr Found %: Br 51.9. $C_{13}H_{17}ON_2Br \cdot 2HBr$. Calculated %: Br 52.3

[Quinuclidyl-(2)]-[pyridyl-(2)]-ketone (IV)

To a mixture of 2.85 g {β-[piperidyl-(4)]-α-bromoethyl}-[pyridyl-(2)]-ketone and 40 ml chloroform was added a solution of 3.1 g sodium bicarbonate in 45 ml water. The mixture was shaken for 2 1/2 hours. The chloroform layer was then separated from the aqueous layer, dried with potassium carbonate and left to evaporate at room temperature. Evaporation of the chloroform left a dark-yellow, crystalline powder weighing 1.22 g, m.p. 62.5-67°. After recrystallization from gasoline (90-100° fraction), the substance was obtained in the form of white prisms melting at 71.5-73°. Good solubility in alcohol, acetone, chloroform, ether and hot gasoline. The analytical data agree with the composition [quinuclidyl-(2)]-[pyridyl-(2)]-ketone. Yield 0.71 g (53.7%).

4.477 mg substance: 11.819 mg CO_2; 2.904 mg H_2O. 3.712 mg substance: 9.841 mg CO_2; 2.428 mg H_2O. Found %: C 72.00, 72.30; H 7.25, 7.32. $C_{13}H_{16}ON_2$. Calculated %: C 72.18; H 7.46.

[Quinuclidyl-(2)]-[pyridyl-(2)]-carbinol (V)

A solution of 3.19 g quinuclidyl-pyridyl-ketone in 58.9 ml hydrochloric acid (0.1 N) was mixed with 10 ml 2% palladium chloride and subjected to hydrogenation under a pressure of 50-70 cm water column. At the end of the hydrogenation the catalyst was filtered off and the filtrate worked up with excess of 50% KOH. The separated base was extracted with ether and the extract dried with potassium carbonate. The ether was driven off to leave 3.15 g of a mixture of diastereoisomeric racemates of quinuclidyl-pyridyl-carbinol in the form of a crystal mass melting at 69-89°.

3.316 mg substance: 8.741 mg CO_2; 2.492 mg H_2O. 5.970 mg substance: 0.595 ml CH_4 (0°, 760 mm). Found %: C 71.88; H 8.41; OH 7.60. $C_{13}H_{18}O_2N_2$. Calculated %: C 71.51; H 8.31; OH 7.80.

The diastereoisomeric racemates were resolved by taking advantage of the differing solubilities of their hydrochlorides in alcohol.

3.08 g of the mixture of diastereoisomeric racemates of quinuclidyl-pyridyl-carbinol was dissolved in 14 ml absolute alcohol and to the solution was added the amount of 17% alcoholic hydrogen chloride calculated for formation of the monohydrochloride. The resultant precipitate was filtered from mother liquor (mother liquor 1) and washed with absolute alcohol and ether. Yield 1.42 g hydrochloride with m.p. 222.5-225°. After recrystallization from absolute alcohol the hydrochloride melted at 232-233°. White microscopic prisms, readily soluble in water and chloroform, fairly readily soluble in hot alcohol (1 : 16), poorly soluble in cold alcohol (approx. 1 : 80). Analysis of this substance identified it as quinuclidyl-pyridyl-carbinol hydrochloride (hydrochloride of racemate A).

3.558 mg substance: 8.042 mg CO_2; 2.731 mg H_2O. Found %: C 61.64; H 7.49. $C_{13}H_{18}ON_2 \cdot HCl$. Calculated %: C 61.27; H 7.52.

The base (racemate A) was isolated from the hydrochloride and melted at 118-119° after recrystallization from a gasoline fraction (70-90°). White clusters of needles with good solubility in water, alcohol, acetone and chloroform; poor in ether.

4.329 mg substance: 11.386 mg CO_2; 3.068 mg H_2O. Found %: C 71.73; H 8.31. $C_{13}H_{18}ON_2$. Calculated %: C 71.51; H 8.31.

Dihydrochloride: White crystals rapidly deliquescing in the air.

The alcoholic mother liquor from the hydrochloride (mother liquor 1) was evaporated in vacuum, the residue was dissolved in 7 ml absolute alcohol, and the solution diluted with 20 ml dry acetone. 1 g of a precipitate then came down; this was the hydrochloride of the second diastereoisomeric racemate (racemate B) contaminated with the hydrochloride of racemate A. The precipitate was filtered, washed with acetone; m.p. 175-185°. The mother liquor was evaporated in a vacuum, the residue was converted to the base with the help of 50% KOH solution, the base was extracted with ether and the extract dried with potassium carbonate. Removal of the ether left 0.38 g crystals with m.p. 73-79°. Two recrystallizations from gasoline (70-90° fraction) gave 0.26 g substance, as [illegible] fine white prisms, melting at 80-82° (racemate B).

The substance has good solubility in water, alcohol, ether, chloroform and acetone, as well as in hot gasoline.

6.319 mg substance: 16.547 mg CO_2; 4.599 mg H_2O. 5.160 mg substance: 13.601 mg CO_2; 3.729 mg H_2O. Found %: C 71.42, 71.89; H 8.15, 8.08. $C_{13}H_{18}ON_2$. Calculated %: C 71.51; H 8.31.

Monohydrochloride: A white crystalline powder with m.p. 175-177°; readily soluble in water, alcohol and chloroform, poorly in acetone.

Boiling of the prepared racemates (A and B) with 50% acetic acid leads to cleavage of the quinuclidine ring, which process is characteristic of quinine alkaloids, and to conversion into {β-[piperidyl-(4)]-ethyl}-[pyridyl-(2)]-ketone.

SUMMARY

1. [Quinuclidyl-(2)]-[pyridyl-(2)]-ketone was synthesized.

2. Catalytic hydrogenation of this ketone gives a mixture of two diastereoisomeric racemates whose resolution was effected by exploiting the differing solubilities of their hydrochlorides in alcohol.

3. Boiling of the obtained racemates with 50% acetic acid resulted, as with other compounds of the quinine series, in the reaction of "hydraminic cleavage" and formation of {β-[piperidyl-(4)]-ethyl}-[pyridyl-(2)]-ketone.

Both racemates were found to be inactive in tests on siskins infected with Plasmodium relictum.

LITERATURE CITED

[1] M. V. Rubtsov, J. Gen. Chem., 13, 702 (1943); M. V. Rubtsov and V. A. Volskova, J. Gen. Chem., 23, 1685 (1953).*

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*See Consultants Bureau Translation, page 1771.

IMIDAZOLE DERIVATIVES

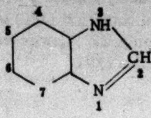
XI. CONDENSATION OF PHTHALIC ANHYDRIDE WITH BENZIMIDAZOLE DERIVATIVES [1]

L. S. Efros, B. A. Porai-Koshits and S. G. Farbenshtein*

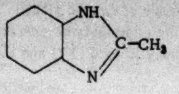
The valuable vat dyes include some derivatives of anthraquinone-containing imidazole rings [2]. They are usually obtained from diaminoanthraquinones whose synthesis is rather complicated. It, therefore, appeared expedient to attempt to prepare such compounds by another route, namely by condensing benzimidazole derivatives with phthalic anhydride. Such was the original purpose of this investigation.

It was found, however, that benzimidazole (I) itself is incapable of entering into condensation with phthalic anhydride. We know that substituents in the 5(6)-position have hardly any influence on the reactivity of benzimidazole [3]: we therefore decided to increase its activity by introducing substituents of the first order into the 2-position.

2-Methyl-benzimidazole (II) also proved incapable of condensation. On the other hand, 2-hydroxybenzimidazole (III) smoothly entered into this reaction and we obtained 5-o-carboxybenzoyl-2-hydroxybenzimidazole (IV), which is readily transformed by treatment with sulfuric acid into the anthraquinone derivative (V).



(I)



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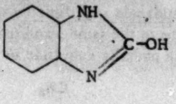

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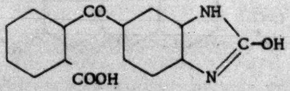

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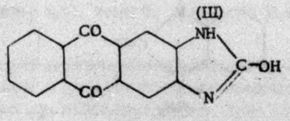
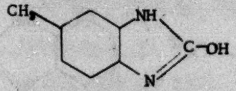


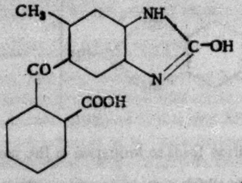
(V)

The structure of this product was confirmed by its synthesis from 2,3-diaminoanthraquinone and carbonyl chloride.

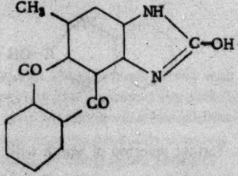
Equally successful was the performance of the reaction between phthalic anhydride and 5-methyl-2-hydroxybenzimidazole (VI), which gave the carboxylic acid (VII) and the anthraquinone derivative (VIII):



(VI)

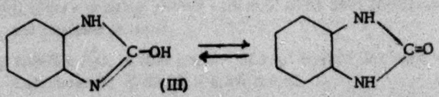


(VII)



(VIII)

As we know [4], 2-hydroxybenzimidazole (III) is tautomeric with o-phenyleneurea (IX)



(III) (IX)

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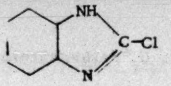
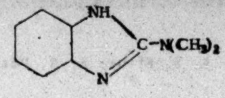
*Deceased

The very low basicity constant that we found in potentiometric titration of this substance [5] ($10^{-10.6}$) indicates that formula (IX) is more correct.

The question, therefore, arose as to which tautomeric form of this compound enters into the reaction under consideration. If it reacts in the form of o-phenyleneurea (IX), then only those benzimidazole derivatives which are susceptible to such a tautomerism should be capable of entering into the Friedel-Crafts reaction. We tested this point by synthesizing, starting from 2-chlorobenzimidazole (X), 2-dimethylaminobenzimidazole (XI) which is not susceptible to such transformations.

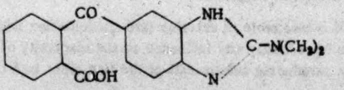


(X)

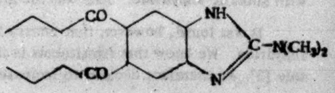


(XI)

It was found that this product smoothly enters into condensation with phthalic anhydride to form the carboxylic acid (XII) which undergoes transformation into the anthraquinone derivative (XIII)

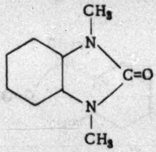


(XII)

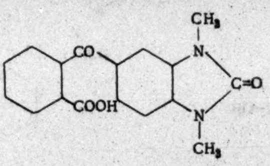


(XIII)

It was interesting to study also the reactivity of the o-phenyleneurea derivative (XI). The N,N-dimethyl derivative (XIV) required for this purpose is, as we established, readily obtained by direct methylation of 2-hydroxybenzimidazole with dimethylsulfate in presence of caustic alkali. The basicity constant of compound (XIV) was found to be of the same magnitude as that of the unmethylated product given above. This compound likewise readily reacted with phthalic anhydride to form the carboxylic acid (XV) and the anthraquinone derivative (XVI)



(XIV)



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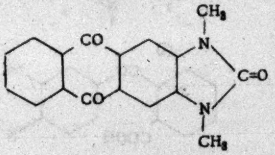
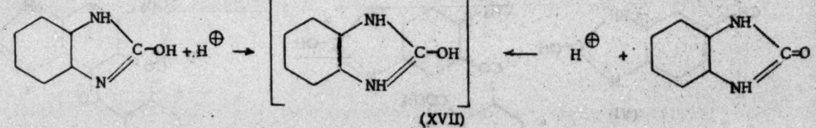


(XVI)

Consequently, both of the tautomeric forms of 2-hydroxybenzimidazole are equally capable of smoothly condensing in the same direction with phthalic anhydride.

We explain this behavior by the fact that in the reaction conditions both tautomers form one and the same cation (XVII)



(XVII)

further reaction of which with phthalic anhydride leads to formation of the products described above.

Only those derivatives of benzimidazole which contain an active substituent of the first order in the 2-position are capable of entering into this reaction.

EXPERIMENTAL*

1. Starting Products

Benzimidazolone [6]. 24.6 g dry o-phenylenediamine hydrochloride is thoroughly triturated in a mortar with 10 g urea and the mixture is heated in a beaker on a paraffin wax bath to 150°. The mixture melts at first but after a short time it again solidifies. The melt is cooled, triturated in a mortar and dissolved in warm, dilute NaOH solution. The solution is filtered and hydrochloric acid is run into the filtrate to precipitate benzimidazolone in the form of fine, faintly yellow leaflets. Yield of product 16 g (about 88%). The product readily crystallizes from alcohol in the form of leaflets with m.p. 308°.

5-Methylbenzimidazolone [7]. Synthesis is performed as for benzimidazolone. From 20 g 3,4-toluenediamine and 20 g urea is obtained 16.5 g (70%) 5-methylbenzimidazolone. After recrystallization from alcohol the m.p. is 292°.

1,3-Dimethylbenzimidazolone. 5 g benzimidazolone is dissolved in 40 ml 7.5% NaOH and at 60° with intensive stirring addition is made dropwise to the solution of 7.5 ml dimethylsulfate and 13 ml 25% alkali. A considerable amount of oil then rises to the surface of the mass in the flask. The solution is brought to the boil and refluxed for 1½ hours. The mass in the flask is then cooled with ice and salt and the solidifying reaction product is filtered off. The precipitate is crystallized from 150 ml water in presence of animal charcoal. The resultant long, colorless needles contain water of crystallization. Yield 4.3 g (71%). After drying in a vacuum-desiccator, the product is crystallized from ligroine. Fine prisms with m.p. 106.5-107°.

0.1443 g sub.: 21.8 ml N_2 (23°, 757 mm). Found %: N 17.20. $C_9H_{10}ON_2$. Calculated %: N 17.27.

2-Chlorobenzimidazole. 1.34 g benzimidazole, 6.7 ml phosphorus oxychloride and 2-3 drops concentrated hydrochloric acid are heated in a sealed tube for 3 hours at 160-170°. The excess phosphorus oxychloride is driven off from the resultant dark-brown solution in vacuum and the residue is carefully decomposed with ice water. The liquid is filtered from impurities and the filtrate neutralized with ammonia. A further crop of whitish needles of 2-chlorobenzimidazole is obtained from the weakly acid solution and is collected and purified by crystallization from aqueous alcohol. Lustrous, colorless leaflets with m.p. 212-215°. Yield 1.2-1.4 g. The product is soluble in dilute inorganic acids and in solutions of caustic alkalies.

0.1015 g sub.: 15.9 ml N_2 (18°, 762 mm). 0.0969 g sub.: 0.0929 g AgCl. Found %: N 18.42; Cl 23.42. $C_7H_5N_2Cl$. Calculated %: N 18.37; Cl 23.28.

2-Dimethylaminobenzimidazole. 3 g 2-chlorobenzimidazole, 3.25 g dimethylamine hydrochloride and 2.24 g KOH in 30 ml water are heated in a sealed tube at 150-160° for 5-6 hours. A light-grey precipitate comes down after cooling of the reaction mass and is filtered, washed with water and crystallized from alcohol. Yield 2.6-2.7 g (80%). Colorless microscopic prisms with m.p. 314-316°.

0.0992 g sub.: 22.7 ml N_2 (23°, 758 mm). Found %: N 26.31. $C_9H_{11}N_3$. Calculated %: N 26.07.

The product is readily purified also in the form of the hydrochloride which comes down from solution in the form of lustrous needles with m.p. 291°.

0.1085 g sub.: 19.3 ml N_2 (16°, 760 mm). 0.1235 g sub.: 6.25 ml 0.1 N NaOH. Found %: N 21.01; Cl 17.97. $C_9H_{11}N_3 \cdot HCl$. Calculated %: N 21.25; Cl 17.98.

2. Preparation of Anthraquinone Derivatives

a) **From benzimidazolone.** 3 g pure benzimidazolone and 3.4 g sublimed phthalic anhydride are mixed with 50 ml tetrachloroethane in a round-bottomed flask fitted with reflux condenser, stirrer and thermometer; the phthalic anhydride dissolves and the benzimidazolone remains in the form of a suspension. 10 g anhydrous aluminium chloride is added in the cold and the mass is heated to 90° with stirring. The aluminium chloride gradually dissolves and the contents acquire a dark, reddish-violet color. With progressive heating the color of the solution becomes lighter and a dark resin forms on the sides. After 3½ hours, the evolution of hydrogen chloride abates and the mixture, acidified with hydrochloric acid, is poured into a flask. The tetrachloroethane is distilled in steam and the reaction product is filtered (IV). Weight 3.57 g. Repeated reprecipitations from the sodium carbonate solution with hydrochloric acid followed by washing gives a colorless product with m.p. about 300°, readily soluble in glacial acetic acid, less readily in alcohol, and insoluble in water.

0.2838 g sub.: 0.6545 g CO_2; 0.0975 g H_2O. 0.3608 g sub.: 31.2 ml N_2 (23°, 762 mm). Found %: C 62.94; H 3.84; N 9.89. $C_{15}H_{10}O_4N_2$. Calculated %: C 63.83 H 3.57; N 9.93.

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* N. A. Zakharova and S. Lotareichik took part in the experimental work

Cyclization of the benzoylbenzoic acid derivative (IV) to the anthraquinone derivative (V) is effected by heating 8 g of the product in solution with 70 ml concentrated sulfuric acid for one hour on a boiling water bath. The solution is poured into 300 ml water and the yellow reaction product is filtered off. Yield nearly quantitative. The product is easily purified by converting it to the vat. It is purified for analysis by crystallizing from quinoline or pyridine. Bright-yellow needles with m.p. above 350°.

0.1368 g sub.: 0.3396 g CO_2; 0.0520 g H_2O. 0.1897 g sub.: 17.2 ml N_2 (22°, 762 mm). 0.1285 g sub.: 11.6 ml N_2 (22°, 760 mm). Found %: C 67.75; H 4.25; N 10.4, 10.35. $C_{15}H_8O_3N_2$. Calculated %: C 68.18; H 3.05, N 10.60.

b) From 5-methylbenzimidazolone. The condensation is performed exactly as in the preceding case. From 10 g 5-methylbenzimidazolone and 10 g phthalic anhydride is obtained 12.8 g of benzoylbenzoic acid derivative (64% of the theoretical). The product is purified by crystallization from acetic acid. M.p. 294°.

0.1031 g sub.: 8.9 ml N_2 (25°, 754 mm). Found %: N 9.71. $C_{16}H_{12}O_4N_2$. Calculated %: N 9.46.

Cyclization to the anthraquinone derivative (VIII) is performed in sulfuric acid. The yield is nearly quantitative. Purification by crystallization from quinoline. Fine yellow needles melting at above 350°.

0,643 g sub.: 0.1623 g CO_2; 0.0222 g H_2O. 0.0778 g sub.: 7.2 ml N_2 (24°, 760 mm). Found %: C 68.88; H 3.86; N 10.52. $C_{16}H_{10}O_3N_2$. Calculated %: C 69.06; H 3.62; N 10.07.

c) From 1,3-dimethylbenzimidazolone. Condensation of 3 g product with 3 g phthalic anhydride in similar conditions gives 3,8 g benzoylbenzoic acid derivative (XV), which crystallizes well from aqueous acetic acid in the form of fine, faintly yellow needles with m.p. 268°.

0,2891 g sub.: 23.7 ml N_2 (23°, 755 mm). Found %; N 9.28. $C_{17}H_{14}O_4N_2$. Calculated %: N 9.03.

Cyclization of the product (XV) to the anthraquinone derivative (XVI) is performed in sulfuric acid. The yield is nearly quantitative. Purification by crystallization from glacial acetic acid. Long, bright-yellow needles melting at above 350°.

0.1018 g sub.: 8.6 ml N_2 (22° 762 mm). Found %: N 9.67. $C_{17}H_{12}O_3N_2$. Calculated %: N 9.59.

d) From 2-dimethylaminobenzimidazole. Condensation of 3 g product with 3 g phthalic anhydride gives 3.5 g benzoylbenzoic acid derivative (XII). After driving off the tetrachloroethane, the hydrochloride of this product collects in the form of a resin on the walls of the flask. The liquid is poured off and the product is dissolved in 70 ml hot water; the base is precipitated by adding sodium acetate. The product is washed and reprecipitated from its solution in sodium carbonate with acetic acid. Fine needles with a faint orange-to-pink color.

Without further purification the substance is treated with concentrated sulfuric acid and converted into the anthraquinone derivative (XIII). On pouring the sulfuric acid solution into water, the bright-yellow sulfate comes down (being poorly soluble in cold water). The product is purified by crystallizing its hydrochloride from water. The fine yellow needles of this salt melt at above 360° in a capillary. The base (orange-yellow) is insoluble in organic solvents. On heating it dissolves in aqueous caustic alkalies and its salt comes down on cooling.

0.1289 g sub.: 14.6 ml N_2 (22°, 760 mm). 0.1252 g sub.: 13.8 ml N_2 (22°, 764 mm). Found %: N 13.09, 12.82. $C_{17}H_{13}O_2N_3 \cdot HCl$. Calculated %: N 12.82.

SUMMARY

Out of a number of derivatives of benzimidazole, only those containing an active substituent of the first order in the 2-position are capable of entering into condensation with phthalic anhydride in presence of aluminum chloride. Among such compounds are benzimidazolone, 1,3-dimethylbenzimidazolone and the 2-dimethylamino derivative. All these compounds apparently react in the form of the corresponding cations.

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* See Consultants Bureau Translation, page 1289.

** See Consultants Bureau Translation, page 995.

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* See Consultants Bureau Translation, page 725.

REACTIONS OF 6-QUINOLINECARBOXALDEHYDE

B. P. Lugovkin

The chemical properties of the quinoline aldehydes, due to the difficulty of synthesis, have been little studied.

Thanks, however, to the work of V. M. Rodionov and M. A. Berkengeim, published in 1944 [1], the synthesis of some aldehydes, including 6-quinoline carboxaldehyde today does not present any special difficulties.

They obtained the aldehyde in a yield of up to 60% by oxidation of 6-methylquinoline with selenium dioxide at 150-210°

G. A. Melentyeva and S. I. Kanevskaya [2] have recently studied the aldol condensation of 6-quinolinecarboxaldehyde with nitroalkanes (nitroethane and α-nitropropane) followed by catalytic reduction of quinolyl-6-nitroalklanes to quinolyl-6-alkanolamines, which were identified in the form of their dihydrochlorides.

In view of the definite interest in the study of quinoline derivatives, we have investigated a whole series of reactions of 6-quinolinecarboxaldehyde synthesized by the method of Rodionov and Berkengeim.

We oxidized the aldehyde with selenium dioxide and found that the product of oxidation is quinoline-6-carboxylic acid in a yield up to 64% of the theoretical. The reaction takes place very violently at above 240°.

By treating the aldehyde with concentrated aqueous KOH (Cannizzaro reaction) we effected the previously unreported synthesis of 6-quinolyl alcohol in the form of colorless crystals with m.p. 81-82°, in a yield of 74% of the theoretical. Quinoline-6-carboxylic acid was isolated in a yield of up to 94% of the theoretical.

Heating of 6-quinolyl alcohol with methyl iodide, ethyl bromide and ethyl iodide led to the corresponding alkyl halides of the alcohol.

Resinous products were formed when an attempt was made to carry out the acyloin condensation of 6-quinolinecarboxaldehyde with potassium cyanide; 6,6'-quinoloin was extracted in insignificant amount (up to 5%) in the form of colorless crystals* with m.p. 167°. It is reported in the literature that some aromatic aldehydes such as, for example, amino- and nitrobenzaldehydes, do not give the corresponding benzoins [3].

We also condensed 6-quinolinecarboxaldehyde with primary aromatic amines. The Schiff bases of 6-quinolideneaniline and o-toluidine are described in the literature [4].

By heating the aldehyde with α-aminopyridine in alcoholic solution, we synthesized 6-quinolidene-α-aminopyridine in the form of colorless crystals with m.p. 139-140° in a yield of 86.4% of the theoretical. Heating with methyl iodide and ethyl iodide led to the corresponding dialkyl iodides.

Reaction of the aldehyde with β-naphthylamine gave 6-quinolidene-β-naphthylamine in the form of colorless crystals with m.p. 140-141°, in a yield of 90% of the theoretical. Its methiodide and ethiodide were synthesized.

Reaction with α-naphthylamine gave 6-quinolidene-α-naphthylamine in the form of an oily liquid in a yield of 83% of the theoretical. It was characterized as the picrate with m.p. 195-196°.

Reaction of the aldehyde (2 moles) with o-phenylenediamine gave 6,6'-diquinolidene-o-phenylenediamine in the form of pale-green crystals with m.p. 221-222°; yield 38% of the theoretical.

Reaction of the aldehyde (2 moles) with p-phenylenediamine gave 6,6'-diquinolidene-p-phenylenediamine in the form of light-green crystals with m.p. 252-253°, in a yield of 92% of the theoretical.

The product of reaction of 6-quinolinecarboxaldehyde (2 moles) with benzidine was 6,6'-diquinolidene-benzidine; yellow crystals with m.p. 262-264°; yield 84% of theory.

The constants of the synthesized 6-substituted quinolines are set forth in the table.

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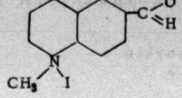
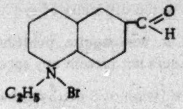
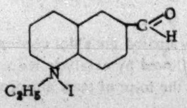
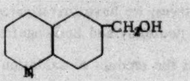
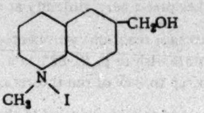
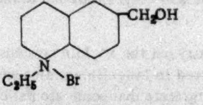
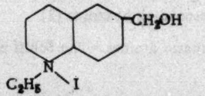
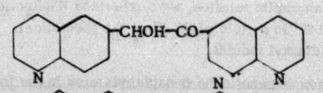
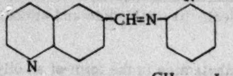
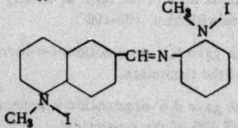
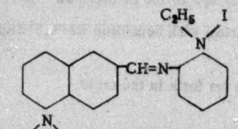
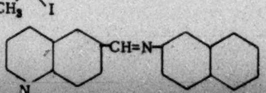
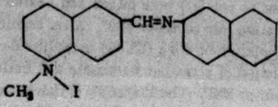
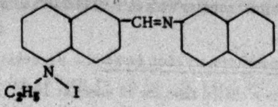
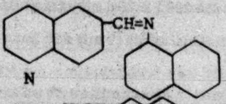
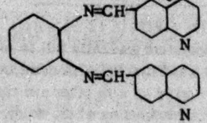
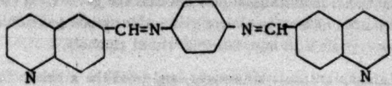
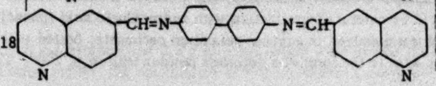
* After thorough purification, benzoin is colorless [3].

No. of Prep.	Formula	Melting point (°C)	Yield (in %)	Remarks
1		222	66	Literature, m.p. 218°
2		191-192	64	
3		195-196	80	
4		81-82	74	Picrate, m.p. 201-202°
5		170	66	
6		177-178	95	
7		132	91	
8		166-167	5	Picrate, m.p. 237-238°
9		139-140	86	
10		126-128	81	
11		119-120	53.6	
12		140-141	90	

No. of Prep.	Formula	Melting point (°C)	Yield (in %)	Remarks
13		210-214	85	
14		183-185	52	
15		Oily liquid	84	Picrate, m.p. 195-196°
16		221-222	38	
17		252-253	92	
18		262-264	84	

EXPERIMENTAL

In all the experiments anhydrous 6-quinolinecarboxaldehyde (m.p. 74-76°) was used; it is soluble in water, alcohol, ether, dioxane, benzene and acetic acid The picrate is prepared in alcoholic solution; after recrystallization from glacial acetic acid it forms dark-yellow crystals with m.p. 196-197°.

Action of Alkyl Halides on 6-Quinolinecarboxaldehyde

0.5 g aldehyde and 0.8 g methyl iodide were heated on a water bath at 85-90° for 30 minutes. After evaporating off the methyl iodide, the 6-quinolinecarboxaldehyde methiodide was repeatedly washed with absolute alcohol and dry ether; yield 0.62 g (65.9%) of yellow crystals with m.p. 222° [4]. The crystals readily dissolve in water; insoluble in ether and sparingly soluble in absolute alcohol.

0.0966 g sub.: 0.0758 g AgI. Found %: I 42.42. $C_{11}H_{10}ONI$. Calculared %: I 42.45.

0.8 g aldehyde and 1 ml ethyl bromide were heated in a sealed tube at 100-110° for 3 hours. After evaporating off the ethyl bromide, the ethobromide was repeatedly washed with dioxane while heating. Yield 0.87 g (64.0%) of pinkish crystals with m.p. 191-192°; no change in m.p. after repeated washing. Easily soluble in water, alcohol, glacial acetic acid; sparingly in dioxane.

0.0958 g sub.: AgBr 0.0670 g. Found %: Br 29.76. $C_{12}H_{12}ONBr$. Calculated %: Br 30.04.

0.5 g aldehyde and 0.8 g ethyl iodide were heated on a boiling water bath for 30 minutes. After evaporating the ethyl iodide, the ethiodide of the aldehyde was repeatedly washed with benzene and dry ether with heating. Yield 0.8 g (80%) dark-yellow crystals with m.p. 195-196°. Readily soluble in absolute alcohol and water; insoluble in benzene, dioxane, and dry ether.

0.1032 g sub.: 0.0776 g AgI. Found %: I 40.65. $C_{12}H_{12}ONI$. Calculated %: I 40.55.

Oxidation of 6-Quinolinecarboxaldehyde with Selenium Dioxide

5 g aldehyde and 2.5 g selenium dioxide (ground to powder) were mixed and heated in Wood's alloy; at 240° a very violent reaction commenced and the temperature rose to above 300°. After cooling, the mass was washed with water; lengthy extraction with alcohol led to isolation of 3.5 g (63.5%) quinoline-6-carboxylic acid with m.p. 278-280°. The acid was dissolved in an aqueous solution of potassium carbonate and boiled with active carbon; appropriate working-up gave colorless crystals with m.p. 290°. The literature [5] gives m.p. 290-292°. The picrate is prepared in alcoholic solution and forms small yellow needles with m.p. 239-240°; after recrystallization from glacial acetic acid the m.p. is 240-241°.

Action of Alkyl Halides on 6-Quinolinecarboxylic Acid

1 g acid and 5 ml ethyl bromide were heated in a sealed tube for 10 hours at 100°. After evaporation of the ethyl bromide, the original acid was obtained with m.p. 284-286°; mixed melting point 288°.

Heating of the acid (1 g) in the same conditions with ethyl iodide (2 ml) also gave the original acid; m.p. 288°.

Action of Aqueous KOH Solution on 6-Quinolinecarboxaldehyde

To 20 g aldehyde was added an aqueous solution of KOH (16 g KOH in 12 ml water). With thorough stirring the temperature was raised from 20 to 75°; on cooling, the temperature gradually fell to room temperature. After 6 hours the product was filtered in vacuum. The solid product was extracted with ether in an extractor until the 6-quinolyl alcohol was completely extracted (the filtrate was worked up with ether and the ethereal solution added to the main ethereal extract; the alkaline solution was treated for extraction of the acid). After driving off the ether, the residue, in form of orange, lustrous plates, was washed with water until neutral. Yield 8.8 g 6-quinolyl alcohol with a broad melting range (up to 77°). Fractional recrystallization from dioxane gave 7.5 g (74.1%) of pale-yellow crystals with m.p. 81°. Recrystallization from alcohol in presence of active carbon gave colorless crystals with m.p. 81-82°. The picrate forms yellow crystals with m.p. 201-202° (from alcohol).

From the solid residue (after extraction of the alcohol), dissolved in water, and from the alkaline filtrate was isolated 10.3 g (93.6%) of 6-quinolinecarboxylic acid by careful neutralization with hydrochloric acid (phenolphthalein and methyl orange). M.p. 287-288°. The acid was dissolved in aqueous potassium carbonate, boiled with active carbon and worked up to 6-quinolinecarboxylic acid in the form of a colorless powder with m.p. 290°. The picrate melted at 240-241°.

Analysis of the alcohol (Kjeldahl*): 0.4542 g sub.: 24.6 ml NaOH (T 1.0964). Found %: N 8.32. $C_{10}H_9ON$. Calculated %: N 8.81.

Action of Alkyl Halides on 6-Quinolyl Alcohol

0.5 g alcohol and 0.75 g methyl iodide were heated on a boiling water bath for 2 hours. The methyl iodide was driven off and the 6-quinolyl alcohol methiodide was repeatedly washed with dry ether. Yield 0.62 g (66%) yellow crystals with m.p. 164-166°. After recrystallization from alcohol, m.p. 170°; readily soluble in water, very sparingly in dioxane and dry ether.

0.0912 g sub.: 0.0708 g AgI. Found %: I 41.97. $C_{11}H_{12}ONI$. Calculated %: I 42.16.

0.5 g alcohol and 1 ml ethyl bromide were heated in a sealed tube at 90° for 3 hours. After driving off the ethyl bromide, the ethobromide of the alcohol was repeatedly washed with dry ether. Yield 0.8 g (95.2%) of rather dirty crystals with m.p. 166-170°. Recrystallization from dioxane and alcohol (a little) gave light-orange crystals with m.p. 177-178°. Readily soluble in water and alcohol; insoluble in dioxane and dry ether.

0.0965 g sub.: 0.0678 g AgBr. Found %: Br 29.90. $C_{12}H_{14}ONBr$. Calculated %: Br 29.82.

0.5 g alcohol and 1 g ethyl iodide were heated on a boiling water bath for 2 hours. After driving off the ethyl iodide, the ethiodide of the alcohol was repeatedly washed with dry ether. Yield 0.9 g (91%) yellow crystals with m.p. 120-131°. Recrystallization from dioxane and alcohol (in small amount) gave m.p. 132°. Readily soluble in alcohol and water; insoluble in dry ether and dioxane.

0.1122 g sub.: 0.0843 g AgI. Found %: I 40.61. $C_{12}H_{14}ONI$. Calculated %: I 40.29.

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* Metallic mercury was added after heating for several days; during the distillation of the ammonia, zinc dust was added [H. Meyer, Determination of structure of organic compounds. State Sci.-Tech. Press, 129 (1935)].

The Acyloin Reaction

Expt. I. To 12 g 6-quinolinecarboxaldehyde, dissolved in 25 ml alcohol, was added 2.5 g potassium cyanide in 3 ml water. The solution became dark-brown after heating for 30 minutes on the boiling water bath. On pouring into water (200 ml) a resinous, dark-orange precipitate came down; the precipitate was filtered, treated several times with water at the boil (in this treatment an insignificant amount of unchanged 6-quinolinecarboxaldehyde came down from the aqueous solution), dissolved in alcohol and repeatedly digested with active carbon.

Removal of the ethanol left 1 g (8.3%) dark-yellow crystals with m.p. 157-159°. Two recrystallizations from alcohol gave colorless crystals with m.p. 166-167°; yield 0.6 g (50%). The picrate forms light-yellow crystals with m.p. 237-238° (from alcohol).

Expt. II. To 10 g aldehyde, dissolved in 50 ml alcohol, was added 2.5 g potassium cyanide in 3 ml water. Heating was carried out for an hour on the boiling water bath; subsequent treatment gave similar results.

0.1134 g sub.: 6.40 ml NaOH (T 1.0964). Found %: N 8.67. $C_{20}H_{14}O_2N_2$. Calculated %: N 8.92.

Action of α-Aminopyridine on 6-Quinolinecarboxaldehyde

3.9 g aldehyde and 2.4 g α-aminopyridine were heated in alcoholic solution (10 ml) at the boil (on a water bath) for 2 hours. Fractional recrystallization from alcohol (while evaporating) gave 5 g (86.4%) 6-quinolidene-α-aminopyridine in the form of colorless crystals with m.p. 138-139°. After a second recrystallization the m.p. was 139-140°. Sparingly soluble in benzene and water, readily in alcohol, glacial acetic acid and dioxane.

0.1572 g sub.: 18.75 ml NaOH (T 1.0964). Found %: N 18.32. $C_{15}H_{11}N_3$. Calculated %: N 18.03.

Action of Alkyl Halides on 6-Quinolidene-α-aminopyridine

1 g substance and 3.2 g methyl iodide were heated on a boiling water bath for 3 hours. After evaporation of the methyl iodide, the dimethiodide of 6-quinolidene-α-aminopyridine was repeatedly washed with dioxane while heating. Yield 1.8 g (81.1%) of light-yellow crystals with indefinite m.p. 119-120°. On recrystallization from glacial acetic acid, m.p. 126-128° (sintering at 136-139°). Readily soluble in water and alcohol, sparingly in dioxane.

0.0898 g sub.: 0.0818 g AgI. Found %: I 49.24. $C_{17}H_{17}N_3I_2$. Calculated %: I 49.10.

0.6 g substance and 3.3 g of ethyl iodide were heated on a boiling water bath for 2 hours. After evaporation of the ethyl iodide, the diethiodide of 6-quinolidene-α-aminopyridine was repeatedly washed with dioxane while heating. Yield 0.75 g (53.6%) of dark-yellow crystals with m.p. 119-120° (sintering at 122-124°). Soluble in water and alcohol, sparingly soluble in dioxane.

0.0960 g sub.: 0.0828 g AgI. Found %: I 46.63. $C_{19}H_{21}N_3I_2$. Calculated %: I 46.57.

Action of β-Naphthylamine on 6-Quinolinecarboxaldehyde

3 g aldehyde and 2.7 g β-naphthylamine were heated in alcoholic solution (10 ml) at the boil on a water bath for 2 hours. Crystals came down after cooling. Yield 4.75 g 6-quinolidene-β-naphthylamine. From the mother liquor was isolated a further 0.1 g of substance in the form of lustrous plates with m.p. 140-141°. The m.p. did not change after recrystallization. Soluble in alcohol and dioxane, insoluble in water.

0.4854 g sub.: 29.9 ml NaOH (T 1.0964). Found %: N 9.46. $C_{20}H_{14}N_2$. Calculated %: N 9.93.

Action of Alkyl Halides on 6-Quinolidene-β-naphthylamine

0.55 g substance and 1.8 g methyl iodide were heated in a sealed tube at 100° for 2 hours. After evaporation of the methyl iodide, the methiodide of 6-quinolidene-β-naphthylamine was repeatedly washed with dioxane with heating. Yield 0.7 g (85.3%) of dark-yellow crystals with m.p. 210-214° (with sintering). Soluble in alcohol, insoluble in water and dioxane.

0.0802 g sub.: 0.0445 g AgI. Found %: I 30.00. $C_{21}H_{17}N_2I$. Calculated %: I 29.93.

1 g substance and 3 g ethyl iodide were heated on a boiling water bath for 3 hours. After evaporation of the ethyl iodide, the ethiodide of 6-quinolidene-β-naphthylamine was repeatedly washed with dioxane with heating. Yield 0.8 g (51.6%) dark-yellow crystals with m.p. 183-185°, soluble in alcohol, insoluble in water and dioxane.

Action of α-Naphthylamine on 6-Quinolinecarboxaldehyde

3 g aldehyde and 2.7 g α-naphthylamine were heated on a boiling water bath for an hour. An oily liquid was formed with a small content of crystalline material which was filtered off after cooling. Yield 4.5 g (83.5%) 6-

quinolidene-α-naphthylamine.

The same results were obtained in an experiment with heating in alcohol for 2 hours.

To 1.7 g of the aldehyde in 3 ml ethanol was added an alcoholic solution (1.5 mole in 15 ml alcohol) of picric acid; a dark-yellow picrate came down with m.p. 194-195° (from 170° the picrate was green); yield 2.2 g (73.9%). Recrystallization from glacial acetic acid gave fine, golden-yellow needles with m.p. 195-196°.

0.2792 g sub.: 25.70 ml NaOH (T 1.0964).*

Found %: N 14.14. $C_{20}H_{14}N_2 \cdot C_6H_3O_7N_3$. Calculated %: N 13.80.

Action of o-Phenylenediamine on 6-Quinolinecarboxaldehyde

3 g aldehyde (2 moles) and 1 g o-phenylenediamine were heated in alcoholic solution (10 ml) at the boil on a water bath for an hour; after evaporation of the alcohol a crystalline and resinous product were isolated. 5 ml ethanol was added and the crystals were filtered off and washed with alcohol. Yield 1.4 g (37.9%) of di-6,6'-quinolidene-o-phenylenediamine in the form of light-green crystals with m.p. 216-217°. After recrystallization from alcohol, m.p. 221-222°. Crystals badly contaminated with resinous liquid were isolated from the mother liquor after evaporation of the ethanol; no more base could be extracted.

0.3898 g sub.: 38.00 ml NaOH (T 1.0964). Found %: N 14.98. $C_{26}H_{18}N_4$. Calculated %: N 14.51.

Action of p-Phenylenediamine on 6-Quinolinecarboxaldehyde

3 g aldehyde (2 moles) and 1 g p-phenylenediamine were heated in alcoholic solution (20 ml) at the boil for 2 hours; a finely crystalline, yellow product came down. After cooling, the product was filtered and washed with ethanol. Yield 3.4 g (92.1%) of di-6,6'-quinolidene-p-phenylenediamine in the form of light-yellow crystals with m.p. 241-242° (heating from 150° on a metal block). After recrystallization from glacial acetic acid the m.p. was 252-253° (with preliminary contraction). Very sparingly soluble in ethanol and dioxane, soluble in glacial acetic acid.

0.1828 g sub.: 17.10 ml NaOH (T 1.0964). Found %: N 14.37. $C_{26}H_{18}N_4$. Calculated %: N 14.51.

Action of Benzidine on 6-Quinolinecarboxaldehyde

3 g aldehyde and 1.76 g benzidine were heated in alcoholic solution (20 ml) at the boil for 2 hours; a yellow, finely crystalline precipitate was formed. After cooling, the precipitate was filtered and washed with ethanol. Yield 3.7 g (83.9%) di-6,6'-quinolidene-benzidine in the form of yellow, fine crystals with an indefinite melting point. After repeated washings with dioxane (while hot) and recrystallization from glacial acetic acid, the m.p. was 262-264° (heated on metal block from 150°) with preliminary contraction. Very sparingly soluble in alcohol and dioxane, soluble in glacial acetic acid.

0.1834 g sub.: 14.16 ml NaOH (T 1.0964). Found %: N 11.86. $C_{32}H_{22}N_4$. Calculated %: N 12.12.

SUMMARY

1. Reaction of ethyl bromide and ethyl iodide with 6-quinolinecarboxaldehyde gave the corresponding alkyl halide compounds.

2. Oxidation of 6-quinolinecarboxaldehyde with selenium dioxide leads to a very violent reaction with formation of quinoline-6-carboxylic acid.

3. 6-Quinolyl alcohol and 6-quinolinecarboxylic acid were synthesized by the action of concentrated aqueous solution of potassium hydroxide on 6-quinolinecarboxaldehyde. Treatment of the alcohol with methyl iodide, ethyl bromide and ethyl iodide gave the corresponding alkyl halide compounds.

4. The acyloin reaction of 6-quinolinecarboxaldehyde results in much resinification; 6,6'-quinoloin is isolated in insignificant amount.

5. 6-Quinolinecarboxaldehyde was condensed with α-aminopyridine, α- and β-naphthylamines, o- and p-phenylene diamines and benzidine. The corresponding 6-quinolidene-amines and 6,6'-diquinolidene-amines were synthesized.

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*With preliminary reduction with zinc dust in concentrated H_2SO_4.

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*See Consultants Bureau Translation, page 325.

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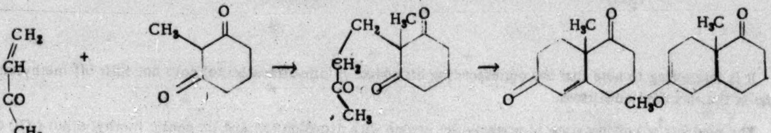
SYNTHESIS OF STEROID COMPOUNDS AND RELATED SUBSTANCES

XXVII. CONDENSATION OF CYCLIC β-DIKETONES WITH VINYL KETONES AND TRANSFORMATIONS OF THE PRODUCTS OF THIS CONDENSATION. II

I. N. Nazarov and S. I. Zavyalov

We recently showed [1] that condensation of methylvinyl ketone (I) with methyldihydroresorcinol (II) gives the triketone (III), cyclization of which leads to 9-methyl-1,6-diketo-$\Delta^{5(10)}$-octalin (IV)

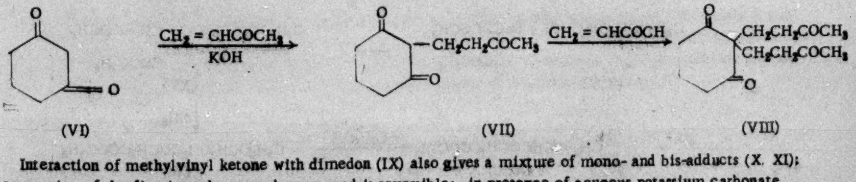


(I) (II) (III) (IV) (V)

The methoxyoctalone (V), similar in structure, has been successfully used in our laboratory for the preparation of steroid compounds of the cis-cis series by the method of diene condensations [2]. The diketooctalin (IV) may present great interest as a starting material for the synthesis of steroid hormones possessing a double bond in the C_4-C_5 position. Whereas the diketooctalin (IV) itself paves the way to synthesis of steroid molecules starting from ring A–B, by suitable choice of vinyl ketone and cyclic β-diketone we can construct a steroid system starting from ring C–D. For this purpose it is necessary to synthesize derivatives of diketodecalin (or 1,5-diketohydrindane) which would have in the 5- (or 4-) position a labile hydrogen or a substituent permitting the attachment of the remaining portion of the steroid molecule to the existing C–D ring system.

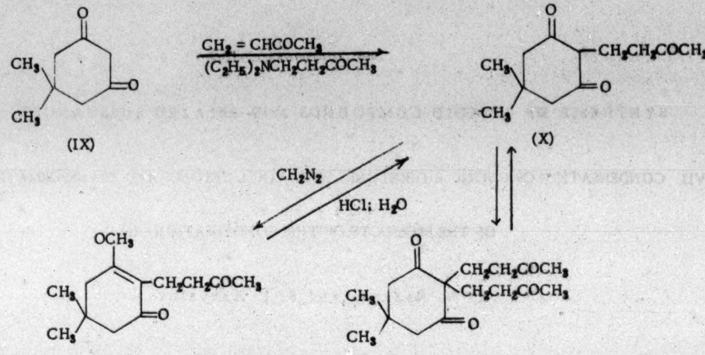
Our present investigation is also devoted to the possibility of synthesizing the bicyclic compounds in question by condensation of vinyl ketones with cyclic β-diketones.

The reaction of methylvinyl ketone with dihydroresorcinol (VI) proceeds smoothly in methanol solution in presence of KOH, but a mixture of approximately equal amounts of the mono- and bis-adducts (VII) and (VIII) is then formed. The mono-adduct (VII) is a high-boiling liquid with strongly marked acidic properties, changing into the bis-adduct (VIII) under the action of methylvinyl ketone. Unlike the methyl derivative (III), which is smoothly converted into the bicyclic compound (IV), (γ-ketobutyl)-dihydroresorcinol (VII) proved to be fairly stable toward cyclizing agents. In presence of sodium alcoholate, phosphorus pentoxide or acetic anhydride, depending upon the temperatures, the substance either does not undergo any change or resinifies.



(VI) (VII) (VIII)

Interaction of methylvinyl ketone with dimedon (IX) also gives a mixture of mono- and bis-adducts (X, XI); the conversion of the first into the second compound is reversible: in presence of aqueous potassium carbonate solution at 80-100° the bis-adduct is reconverted into the monoketobutyl derivative (X).



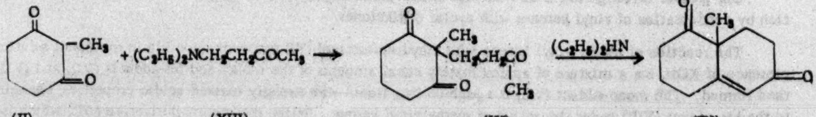
(IX) (X) (XII) (XI)

It is interesting to note that the corresponding bis-adduct of dihydroresorcinol does not split off methylvinyl ketone in the specified conditions.

The products of condensation of methylvinyl ketone with dimedon (X) and its enolic methyl ether (XII) do not give bicyclic compounds under the action of sodium alcoholate or phosphorus pentoxide. As in the case of the dihydroresorcinol derivative (VII), these compounds are either recovered unchanged from the reaction mixture or undergo considerable resinification.

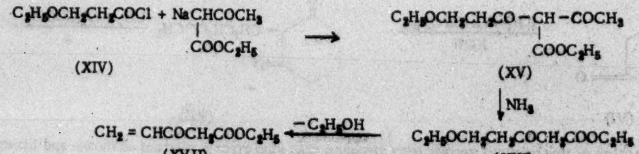
We also tried to synthesize the bicyclic compounds by another method. We subjected dimedon and dihydroresorcinol to the action of 1-diethylamino-3-ketobutane (XIII) at 70-80°. In the case of dimedon, however, we only succeeded in obtaining the above-mentioned mono-adduct (X), while in the case of dihydroresorcinol a complex mixture is obtained from which a carboxylic acid of unknown structure was isolated.

On the other hand, heating of 1-diethylamino-3-ketobutane (XIII) with methyldihydroresorcinol leads directly to formation of 9-methyl-1,6-diketo-$\Delta^{5(10)}$-octalin (IV). This transformation proceeds through the stage of triketone (III) which cyclizes under the influence of diethylamine during the reaction.



(II) (XIII) (III) (IV)

The preparation of 5-carbethoxy-9-methyl-1,6-diketodecalin (XX) required carbethoxymethylvinyl ketone (XVII), whose synthesis was effected by the following scheme:



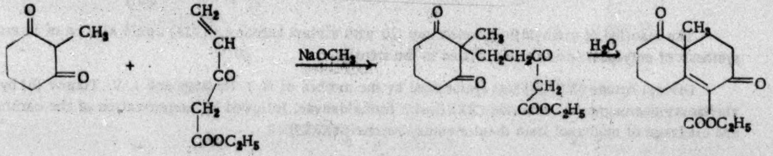
$$\underset{\text{(XIV)}}{C_2H_5OCH_2CH_2COCl} + \underset{\displaystyle COOC_2H_5}{NaCHCOCH_3} \longrightarrow \underset{\text{(XV)}}{C_2H_5OCH_2CH_2CO-\underset{\displaystyle COOC_2H_5}{CH}-COCH_3}$$

$$\xrightarrow{NH_3} \underset{\text{(XVI)}}{C_2H_5OCH_2CH_2COCH_2COOC_2H_5} \xrightarrow{-C_2H_5OH} \underset{\text{(XVII)}}{CH_2 = CHCOCH_2COOC_2H_5}$$

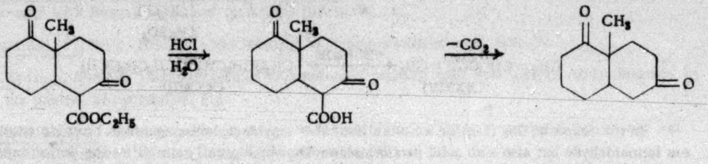
β-Ethoxypropionyl chloride (XIV) reacts with sodium ethylacetoacetate to give the diacyl derivative (XV) which with ammonia undergoes ammonolysis with formation of ethyl γ-(ethoxymethyl)-acetoacetate (XVI).

Distillation of the latter in vacuum in presence of p-toluenesulfonic acid causes cleavage of a molecule of alcohol with formation of vinylcarbethoxymethyl ketone (XVII) Its reaction with methyldihydroresorcinol, which proceeds in presence of sodium methylate with considerable evolution of heat, gives, in addition to the triketo ester (XVIII), the bicyclic diketo ester (XIX). This occurrence of cyclization in the conditions of condensation cannot be regarded as unexpected, for in this case ring closure is facilitated by the presence of an active methylene group in the molecule of the triketo ester (XVIII).

The triketo ester (XVIII) is a pure keto form, since in the cold it does not give a coloration with iron chloride. The triketo ester (XVIII) readily cyclizes when heated with formation of the unsaturated diketo ester (XIX) which, in presence of platinum catalyst is hydrogenated to 5-carbethoxy-9-methyl-1,6-diketodecalin (XX). Structure of the latter was confirmed by subjecting it to saponification and decarboxylation, when a diketone was obtained which was identical with the previously described cis-9-methyl-1,6-diketodecalin (XXI).



(II) (XVII) (XVIII) (XIX)



(XX) (XXI)

In order to introduce the carbomethoxyethyl group into the 5-position of the diketooctalin (IV), we started from (γ-carbomethoxypropyl)-vinyl ketone (XXV), which we synthesized by two methods.

The hydrochloride of γ-(β'-piperidinopropionyl)-butyric acid (XXII) is treated in a medium of methanol with dry hydrogen chloride. The resultant amino ester (XXIII) is transformed into the methiodide (XXIV) which is then subjected to dry distillation.

$$\underset{\text{(XXII)}}{\mathrm{HCl\cdot C_5H_{10}NCH_2CH_2COCH_2CH_2CH_2COOH}} \xrightarrow[\mathrm{HCl}]{\mathrm{CH_3OH}} \underset{\text{(XXIII)}}{\mathrm{C_5H_{10}NCH_2CH_2COCH_2CH_2CH_2COOCH_3}}$$

$$\downarrow \mathrm{CH_3I}$$

$$\underset{\text{(XXV)}}{\mathrm{CH_2 = CHCOCH_2CH_2CH_2COOCH_3}} \longleftarrow \underset{\text{(XXIV)}}{\mathrm{CH_3I\cdot C_5H_{10}NCH_2CH_2COCH_2CH_2CH_2COOCH_3}}$$

In the second method, γ-(ethoxymethyl)-acetoacetic ester (XVI) in presence of sodium methylate is condensed with acrylic ester and the reaction product (XXVI) is saponified and decarboxylated by boiling with hydrochloric acid. The keto acid (XXVII) is esterified with methyl alcohol in presence of hydrogen chloride and the resultant ester (XXVIII) is distilled in vacuum with a small quantity of p-toluenesulfonic acid.

$$\underset{\text{(XVI)}}{\mathrm{C_2H_5OCH_2CH_2COCH_2COOC_2H_5}} \xrightarrow[\mathrm{CH_3ONa}]{\mathrm{CH{=}CHCOOCH_3}} \underset{\text{(XXVI)}}{\mathrm{C_2H_5OCH_2CH_2CO\overset{COOC_2H_5}{C}HCH_2CH_2COOCH_3}}$$

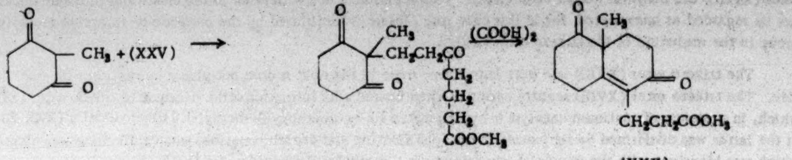
$$\xrightarrow[\mathrm{H_2O}]{\mathrm{HCl}} \underset{\text{(XXVII)}}{\mathrm{C_2H_5OCH_2CH_2COCH_2CH_2CH_2COOH}},$$

$$\underset{\text{(XXVIII)}}{\mathrm{C_2H_5OCH_2CH_2COCH_2CH_2COOCH_3}} \xleftarrow[\mathrm{HCl}]{\mathrm{CH_3OH}} \text{(XXVII)}$$

$$\downarrow -\mathrm{C_2H_5OH}\ (\mathrm{C_7H_7SO_3H})$$

$$\mathrm{CH_2{=}CHCOCH_2CH_2CH_2COOCH_3}\ \text{(XXV)}$$

(γ-Carbomethoxypropyl)-vinyl ketone (XXV) adds on to methyldihydroresorcinol under the influence of sodium methylate in methanol solution. Heating of the reaction product (XXIX) in vacuum with oxalic acids gives a crystalline substance with a neutral reaction whose elementary composition exactly corresponds to the bicyclic compound (XXX). It is interesting to note that the triketo ester (XXIX), unlike the triketone (III), does not undergo cyclization when heated with salts of secondary amines at 90-95°.



(XXIX) (XXX)

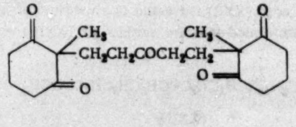
The reaction of methyldihydroresorcinol (II) with divinyl ketone (XXXIV) could also be of interest for the synthesis of polycyclic compounds related to the steroids.

Divinyl ketone (XXXIV) was synthesized by the method of N. I. Nazarov and L. V. Torgov [3] by reaction of vinylacetylenemagnesium bromide (XXXI) with formaldehyde, followed by isomerization of the carbinol (XXXII) and cleavage of methanol from the dimethoxy ketone (XXXIII).

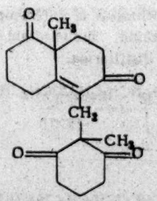
$$\begin{tikzcd} \underset{(XXXI)}{CH_2=CHC\equiv CMgBr} \arrow[r, "(CH_2O)x"] & \underset{(XXXII)}{CH_2=CH-C\equiv CCH_2OH} \arrow[d, "CH_3OH, HgSO_4"] \\ \underset{(XXXIV)}{CH_2=CHCOCH=CH_2} & \underset{(XXXIII)}{CH_3OCH_2CH_2COCH_2CH_2OCH_3} \arrow[l, "-2CH_3OH"'] \end{tikzcd}$$

In the course of this reaction we established that vinylacetylenemagnesium bromide reacts not only with gaseous formaldehyde but also with solid paraformaldehyde, which greatly simplifies the performance of the synthesis.

Addition of methyldihydroresorcinol in ordinary conditions to divinyl ketone (XXXIV) gives a crystalline bis-adduct (XXXV). Due, however, to the instability of the substance we were unable to effect its cyclization to the tricyclic ketone (XXXVI)

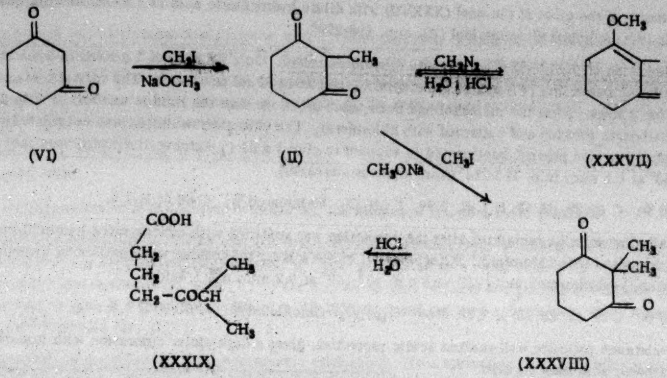


(XXXV)



(XXXVI)

The methyldihydroresorcinol used in the above-described investigations was prepared by us by methylation of dihydroresorcinol (VI). A closer study of this reaction showed that the low yield of methyldihydroresorcinol (II) was connected with the formation of the dimethyl derivative (XXXVIII). The structure of the latter was confirmed by hydrolytic cleavage to the known γ-isobutyrylbutyric acid (XXXIX) [4] and by comparison of its properties with those of the isomeric enolic methyl ether (XXXVII), which can also be formed in the process of methylation. We showed that the enolic ether (XXXVII), prepared by the action of diazomethane on methyldihydroresorcinol, gives on saponification not the carboxylic acid (XXXIX), but the original diketone (II).



EXPERIMENTAL

Methylvinyl ketone (I) (b.p. 79-80°, n_D^{20} 1.4460) was prepared by hydration of vinylacetylene [5].

γ-(β'-Piperidiniopropionyl)butyric acid hydrochloride (XXII) (m.p. 158-159°) [6] was prepared by reaction of γ-acetylbutyric acid with formaldehyde and piperidine hydrochloride.

Dihydroresorcinol (VI) (m.p. 104-105°) was prepared by hydrogenation of resorcinol [7].

Dimedon (IX) (m.p. 144-145°) was synthesized by reaction of malonic ester with mesityl oxide, followed by saponification of the product of cyclization [8].

Divinyl ketone (XXXIV) was obtained by cleavage of alcohol from β,β'-dimethoxydiethyl ketone and was utilized in the form of a methanol solution (b.p. 25-40° at 70 mm) [3].

β-Ethoxypropionyl chloride (XIV) (b.p. 62-64° at 30 mm) was prepared from β-ethoxypropionic acid and thionyl chloride [9].

Methylation of dihydroresorcinol. To a solution of sodium methylate, prepared from 2.3 g sodium and 25 ml dry methanol, was added with stirring, 11.2 g dihydroresorcinol (VI) followed by 16 g methyl iodide. After heat development had ceased, the mixture was boiled on a water bath for 3 hours. The methanol was driven off in vacuum and 10 ml water was added to the residue. The resultant crystalline precipitate was drained and washed with water. Yield 5 g methyldihydroresorcinol (II) with m.p. 208-209° (from aqueous ethanol).

The filtrate remaining after separation of the methyldihydroresorcinol was extracted 5 times with chloroform; the chloroform solution was evaporated to dryness and the residue fractionated in vacuum to give 0.7 g dimethyldihydroresorcinol (XXXVIII) with b.p. 98-100° at 39-40° at 10 mm (from ligroine).

Found %: C 68.19, 68.40; H 8.56, 8.53. $C_8H_{12}O_2$. Calculated %: C 68.5; H 8.6

Hydrolytic cleavage of dimethyldihydroresorcinol. 3 g dimethyldihydroresorcinol (XXXVIII) and 20 ml diluted (1 : 1) hydrochloric acid were heated on a boiling water bath for 2 hours. The mixture was extracted with ether, and after removal of the ether the residue was distilled in vacuum to give 2 g γ-isobutyrylbutyric acid (XXXIX) with b.p. 143-146° at 4 mm; n_D^{21} 1.4449.

The semicarbazone melted at 183-184° with decomposition (from methanol). The literature gives m.p. 185-185.5° (with decomposition) [4].

Preparation of the methyl ether of methyldihydroresorcinol (XXXVII). To a suspension of 3 g methyldihydroresorcinol (II) in 10 ml ether was added a 3% ethereal solution of diazomethane until the substance dissolved completely. After removal of the solvent the residue was distilled in vacuum.

Yield 2.8 g methyl ether of methyldihydroresorcinol (XXXVII) with b.p. 98-99° at 3 mm; m.p. 43-44° (from n-hexane).

Found %: C 68.15, 68.26; H 8.83, 8.80; $C_8H_{12}O_2$. Calculated %: C 68.5; H 8.6.

Treatment of the ether of the enol (XXXVII) with dilute hydrochloric acid (1 : 1) in the cold quantitatively converted it into methyldihydroresorcinol (II), m.p. 208-209°.

Condensation of methylvinyl ketone with dihydroresorcinol. To a solution of 1 g KOH in 8 ml methanol was added 11 g dihydroresorcinol (VI) and 20 g methylvinyl ketone in 80 ml methanol. The mixture was boiled on a water bath for 3 hours. After the methanol had been taken off in vacuum the residue was mixed with 20 ml saturated potassium carbonate solution and extracted with chloroform. The chloroform solution was evaporated to dryness and the neutral reaction product fractionated in vacuum to give 9 g di-(γ-ketobutyl)-dihydroresorcinol (VIII) with b.p. 140-143° at 0.5 mm; m.p. 123-124° (from aqueous methanol).

Found %: C 66.79, 66.78; H 7.92, 7.99. $C_{14}H_{20}O_4$. Calculated %: C 66.6; H 7.9.

The alkaline solution remaining after the extraction was acidified with concentrated hydrochloric acid (to Congo) and extracted with chloroform. After removal of the solvent the residue was distilled in vacuum to give 7 g (γ-ketobutyl)-dihydroresorcinol (VII) with b.p. 137-140° at 0.2 mm; n_D^{20} 1.5400.

Found %: C 66.00, 66.15; H 7.70, 7.65. $C_{10}H_{14}O_3$. Calculated %: C 65.9; H 7.5.

The substance possesses well-marked acidic properties, gives a dark-violet coloration with iron chloride and displaces carbonic acid from its salts.

Reaction of (γ-ketobutyl)-dihydroresorcinol with methylvinyl ketone. To a solution of 0.1 g KOH in 2 ml methanol is added 2 g (γ-ketobutyl)-dihydroresorcinol (VII) followed by 2 g methylvinyl ketone in 8 ml methanol. The mixture is boiled on the water bath for 3 hours. After driving off the methanol in vacuum, the residue is worked up with saturated potassium carbonate solution and extracted with chloroform. After removal of the solvent, the residue crystallized. Yield 1 g of substance with m.p. 123-124° (from aqueous methanol), which did not give a depression with the above-described di-(γ-ketobutyl)-dihydroresorcinol (VIII).

Condensation of methylvinyl ketone with dimedon. To a solution of 1 g KOH in 8 ml methanol was added 14 g dimedon (IX) and 20 g methylvinyl ketone in 80 ml methanol. The mixture was boiled on the water bath for 3 hours. After working up in the usual manner, the neutral portion yielded 12 g di-(γ-ketobutyl)-dimedon (XI) with m.p. 106-107° (from aqueous methanol).

Found %: C 68.60, 68.49; H 8.84, 8.67. $C_{16}H_{24}O_4$. Calculated %: C 68.6; H 8.6.

From the acidic products was isolated 11 g γ-ketobutyldimedon (X) with m.p. 100-101° (from aqueous methanol).

Found %: C 68.68, 68.71; H 8.75, 8.76. $C_{12}H_{18}O_3$. Calculated %: C 68.6; H 8.6

Reaction of substance (X) with methylvinyl ketone gives the bis-adduct (XI).

Transformation of di-(γ-ketobutyl)-dimedon (XI) into the mono-adduct (X). 2 g di-(γ-ketobutyl)-dimedon (XI) and a solution of 2 g potassium carbonate in 8 ml water were subjected to slow distillation at atmospheric pressure. Methylvinyl ketone (m.p. of semicarbazone 140-141°) was detected in the distillate. The operation was interrupted when 2 g solution remained in the distilling flask. This residue was made acid to Congo with dilute hydrochloric acid (1 : 1) and the precipitate was recrystallized from aqueous methanol. Yield 0.8 g substance with m.p. 100-101°, which did not give a depression with the mono-adduct (X).

Preparation of the methyl ether of (γ-ketobutyl)-dimedon (XII). To 8 g (γ-ketobutyl)-dimedon (X) with stirring was added a 3% ethereal solution of diazomethane until nitrogen ceased to come off. After driving off the solvent, the residue was distilled in vacuum.

There was obtained 7 g methyl ether of (γ-ketobutyl)-dimedon (XII) with b p. 148-151° at 2 mm, m.p. 75-76° (from ligroine-benzene mixture).

Found %: C 69.73, 69.61; H 8.97, 8.96. $C_{13}H_{20}O_3$. Calculated %: C 69.6; H 8.9.

On heating with dilute (1 : 1) hydrochloric acid, the substance was entirely transformed into (γ-ketobutyl)-dimedon (X).

Reaction of 1-diethylamino-3-ketobutane with dimedon. A mixture of 7 g dimedon (IX) and 14 g of 1-diethylamino-3-ketobutane (XIII) was heated on a water bath at 90° for 2 hours. While cooling with ice, the reaction mass was treated with dilute hydrochloric acid (1 : 1) until acid to Congo, and the resultant crystals were drained and washed with benzene to give 2 g with m.p. 100-101° (from aqueous methanol), which did not give a depression with (γ-ketobutyl)-dimedon (X).

Reaction of 1-diethylamino-3-ketobutane with dihydroresorcinol. A solution of 5.3 g dihydroresorcinol (VI) and 7 g 1-diethylamino-3-ketobutane (XIII) in 50 ml dry benzene was subjected to distillation at atmospheric pressure. After driving off 40 ml of the solvent, the residue was made acid to Congo with dilute hydrochloric acid (1: 1) and extracted with benzene. After removal of the solvent, the residue partly crystallized. Yield 1.5 g acid with m.p. 162-163° (from aqueous methanol).

Found %: C 71.38, 71.29; H 7.92, 8.07 g-equiv. 234. $C_{14}H_{18}O_3$. Calculated %: C 71.7; H 7.7 g-equiv. 235.

On hydrogenation with Pt catalyst in methanol, the substance absorbs 1 mole hydrogen.

Reaction of 1-diethylamino-3-ketobutane with methyldihydroresorcinol. A mixture of 3 g methyldihydroresorcinol (II) and 5 g 1-diethylamino-3-ketobutane (XIII) was heated on a water bath at 80-90° for 2 hours. After treatment with dilute hydrochloric acid (1 : 1) and extraction with benzene the product of reaction was fractionated in vacuum to give 0.3 g substance with m.p. 48-50°, which did not give a depression with authentic 9-methyl-1,6-diketo-$\Delta^{5(10)}$-octalin (IV) [1].

Preparation of γ-(ethoxymethyl)-acetoacetic ester (XVI). To a suspension of sodium ethylacetoacetate, prepared from 2.3 g sodium, 13 g ethylacetoacetate and 70 ml absolute ether, dropwise addition was made of 14 g β-ethoxypropionyl chloride in 14 ml absolute ether with cooling (iced water) and stirring. The reaction mixture was left at room temperature for 24 hours and then, after separation of the sodium chloride, saturated with dry ammonia while being cooled with ice. The ethereal solution was washed with dilute hydrochloric acid (1 : 1) and then with 5% sodium carbonate solution. After removal of solvent, it was subjected to fractional distillation in vacuum to give 4.5 g γ-(ethoxymethyl)-acetoacetic ester (XVI) with b.p. 80-84° at 2 mm; n_D^{21} 1.4361.

Found %: C 56.92, 57.01; H 8.55, 8.33; $C_9H_{16}O_4$. Calculated %: C 57.4; H 8.5.

Carbethoxymethylvinyl ketone (XVII). 3 g γ-(ethoxymethyl)-acetoacetic ester (XVI) and 0.04 g p-toluenesulfonic acid were subjected to distillation in vacuum at 18-20 mm. The temperature was held at 120-130°. In these conditions cleavage of the alcohol gradually took place and the reaction product distilled over. Yield 1.8 g carbethoxymethylvinyl ketone (XVII) with b.p. 76-78° at 18 mm; n_D^{20} 1.4585.

Found %: C 58.97, 59.24; H 6.59, 6.72. $C_7H_{10}O_3$. Calculated %: C 59.0; H 7.0.

On prolonged standing the substance polymerizes to a transparent vitreous mass.

Reaction of carbethoxymethylvinyl ketone with methyldihydroresorcinol. To a solution of sodium methylate, prepared from 0.05 g sodium and 15 ml absolute methanol, was added 6.5 g methyldihydroresorcinol (II) followed, with energetic stirring, by 7.5 g carbethoxymethylvinyl ketone (XVII). The mixture began to heat up and continued to do so for about 30 minutes. The reaction was completed by heating on a water bath at 50-55° for 30 minutes. After removal of the methanol in vacuum, the residue was worked up with a solution of 3 g sodium carbonate in 10 ml water and extracted with benzene. The solvent-free reaction product crystallized. Yield 4 g of triketoester (XVIII) with m.p. 113-114° (from methanol).

Found %: C 62.49, 62.52; H 7.64, 7.44. $C_{14}H_{20}O_5$. Calculated %: C 62.7; H 7.5.

In the cold the compound does not give a reaction with iron chloride; on heating to 50-60° a cherry-red color appears.

The mother liquor (6 g) remaining after separation of the crystals of triketoester (XVIII) was distilled in vacuum to give 3.8 g of the bicyclic ester (XIX) with b.p. 170-180° at 0.5 mm; n_D^{22} 1.5208.

Found %: C 66.61, 66.53; H 6.91, 7.18; $C_{14}H_{18}O_4$. Calculated %: C 67.2; H 7.2.

The substance gives a coloration with iron chloride; the 2,4-dinitrophenylhydrazone melts at 208-210° (with decomposition).

Cyclization of the triketoester (XVIII). 4 g of triketoester (XVIII) was distilled in vacuum to give 2 g bicyclic ester (XIX) with b.p. 178-183° at 0.5 mm; n_D^{20} 1.5250.

Found %: C 66.85, 66.84; H 6.96, 7.20. $C_{14}H_{18}O_4$. Calculated %: C 67.2; H 7.2.

The 2,4-dinitrophenylhydrazone melted at 208-210° (with decomposition).

Found %: N 15.35, 15.15. $C_{20}H_{22}O_7N_4$ Calculated %: N 13.1.

Hydrogenation of the bicyclic ester (XIX). 2 g bicyclic ester (XIX) was hydrogenated in 5 ml methanol in presence of platinum oxide at room temperature and normal pressure. In the course of an hour 18 ml hydrogen (1 mole) was absorbed, after which hydrogenation substantially ceased. After freeing from catalyst and solvent, the reaction product was fractionated in vacuum to give 1.2 g 9-methyl-1,6-diketo-5-carbethoxydecalin (XX) with b.p. 158-162° at 1 mm; n_D^{20} 1.5168.

Found %: C 67.06, 66.80; H 8.11, 8.12. $C_{14}H_{20}O_4$ Calculated %: C 66.6; H 7.9.

Saponification of 9-methyl-1,6-diketo-5-carbethoxydecalin (XX). 1.3 g 9-methyl-1,6-diketo-5-carbethoxydecalin (XX) and 20 ml dilute hydrochloric acid (1 : 1) were refluxed for 6 hours. After removal of the volatile products in vacuum, there was a residue of 0.8 g viscous oil from which was obtained 0.3 g of a semicarbazone with m.p. 222-223° (with decomposition), not giving a depression with the bis-semicarbazone of authentic cis-9-methyl-1,6-diketodecalin (XXI) [2]. Decomposition of the semicarbazone with hydrochloric acid yielded the 9-methyl-1,6-diketodecalin itself (XXI) with m.p. 65-67° and not giving a depression with an authentic specimen [2].

Preparation of (γ-carbomethoxypropyl)-vinyl ketone (XXV). 1) Into a mixture of 40 g γ-(β'-piperidinopropionyl)-butyric acid hydrochloride (XXII) and 250 ml dry methanol was passed a stream of dry hydrogen chloride until the solution was saturated. After driving off the excess of alcohol and hydrogen chloride in a low vacuum, the residue was treated (while cooling) with a solution of 20 g NaOH in 50 ml water and extracted with ether. The ethereal solution was mixed with 60 g methyl iodide and stood for 6 hours at room temperature before evaporating to dryness on a water bath. The residual methiodide was subjected to distillation in vacuum. Yield 15 g (γ-carbomethoxypropyl)-vinyl ketone (XXV) with b.p. 70-71° at 2 mm; n_D^{20} 1.4481.

Found %: C 61.37, 61.51; H 7.97, 7.99. $C_8H_{12}O_3$ Calculated %: C 61.5; H 7.7.

The semiçarbazone melts at 187-188°.

Found %: N 19.53, 19.62; $C_9H_{15}O_3N_3$. Calculated %: N 19.7.

2) To a solution of the sodium derivative, prepared from 5 g γ-(ethoxymethyl)-acetoacetic ester (XVI) and 0.2 g sodium, was added 2 g methyl acrylate and the mixture heated for 4 hours at 60-65°. The product of condensation was isolated by saponification by boiling for 5 hours with 20 ml dilute hydrochloric acid (1 : 1). After removal of the volatiles in vacuum, the residue was dissolved in 10 ml methanol and the solution saturated with dry hydrogen chloride before evaporating to dryness in vacuum. The reaction products were distilled at 15 mm in presence of a small amount of p-toluenesulfonic acid. Yield 0.7 g (γ-carbomethoxypropyl)-vinyl ketone (XXV) with b.p. 102-105° at 15 mm; n_D^{26} 1.4490.

The semicarbazone melted at 187-188°.

Preparation of 9-methyl-1,6-diketo-5-(β-carbomethoxyethyl)-$\Delta^{5(10)}$-octalin (XXX). To a solution of sodium methylate, prepared from 0.1 g sodium and 15 ml dry methanol, was added 8.7 g methyldihydroresorcinol (II) and 10 g (γ-carbomethoxypropyl)-vinyl ketone (XXV). The mixture was boiled on a water bath for 6 hours. The solvent was taken off in vacuum and the residue worked up with sodium carbonate solution and extracted with ether. Removal of the latter left 15 g viscous oil (n_D^{22} 1.4860), not distilling without decomposition even in high vacuum. 3 g of the crude condensation product and 1 g oxalic acid were heated at 140-150° for 2 1/2 hours. After cooling, the mixture was worked up with 2 g sodium carbonate and 20 ml water; the crystals were drained and washed with ether. Fractional crystallization from benzene gave 0.4 g 9-methyl-1,6-diketo-5-(β-carbomethoxyethyl)-$\Delta^{5(10)}$-octalin (XXX) with m.p. 168-169°.

Found %: C 68.11, 67.94; H 7.41, 7.31. $C_{15}H_{20}O_4$ Calculated %: C 68.2, H 7.6.

Preparation of vinylethinylcarbinol (XXXII). Into a Grignard solution, prepared from 25 g magnesium, 110 g ethyl bromide and 400 ml absolute ether, was passed 65 g dry vinylacetylene. Then with cooling (ice water) and energetic stirring, 50 g finely crushed paraformaldehyde was introduced in portions. The temperature was held at 25-30° by external cooling. After standing for 12 hours at room temperature, the mixture was worked up with ice and dilute hydrochloric acid (1 : 1). The ether layer was separated and dried with sodium sulfate; the ether was driven off and the residue distilled in vacuum to give 35 g vinylethinylcarbinol (XXXII) with b.p. 57-59° at 12 mm; n_D^{20} 1.4935.

Reaction of divinyl ketone with methyldihydroresorcinol. To a solution of sodium methylate, prepared from 0.05 g sodium and 5 ml dry methanol, was added 7 g methyldihydroresorcinol (II) and 2 g divinyl ketone (XXXIV) in 2 ml methanol. The mixture was boiled on a water bath for 3 hours and then evaporated in a vacuum at 50-60°.

The residue was worked up with sodium carbonate solution and extracted with chloroform. After removal of the solvent the residue partly crystallized to give 1.7 g of bis-adduct (XXXV) with m.p. 100-101°(from aqueous methanol).

Found %: C 68.17, 68.22; H 7.82, 7.75. $C_{19}H_{26}O_5$. Calculated %: C 68.2; H 7.8

SUMMARY

1. It is shown that condensation of dihydroresorcinol (VI) and dimedon (IX) with methylvinyl ketone leads to a mixture of mono- and diketobutyl derivatives (VII, VIII, X, XI). The action of various cyclizing media upon the mono-ketobutyl derivatives (VII, X) failed to give the corresponding bicyclic diketones (1,6-diketooctalins).

2. It was established that in the reaction of 1-diethylamino-3-ketobutane (XIII) with dimedon formation takes place of the monoketobutyl derivative (X), while the reaction of the same ketoamine with methyldihydroresorcinol (II) gives 9-methyl-1,6-diketo-$\Delta^{5(10)}$-octalin (IV).

3. Methods are described for the preparation of carbethoxymethylvinyl ketone (XVII) and (γ-carbomethoxypropyl)-vinyl ketone (XXV). Their condensation was effected with methyldihydroresorcinol, leading to ring-closure to form the substituted diketooctalins (XIX, XXX).

4. It was established that the bis-adduct (XXXV) is formed in the reaction of divinyl ketone with methyldihydroresorcinol.

5. The methylation of dihydroresorcinol was studied and it was observed that the dimethyl derivative (XXXVIII) is formed side by side with methyldihydroresorcinol.

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*See Consultants Bureau Translation, page 309.

the residue was worked up with sodium carbonate solution and extracted with chloroform. After removal of the solvent the residue, on chromatography, [illegible] gave 1.2 g of [illegible] (XXXV) with m.p. [illegible] (from [illegible]).

Calculated %: C [illegible]. [illegible]

SUMMARY

1. It is shown that condensation of [illegible] (I) and [illegible] (II) with [illegible] leads to a mixture of mono- and [illegible] (VII, VIII, XI). The action of [illegible] [illegible] failed to give the corresponding [illegible].

2. It was established that in the reaction of [illegible] (IX) with [illegible] takes place of [illegible] (X), while the reaction of the same [illegible] with [illegible] [illegible] (XV).

3. [illegible] of the [illegible] (XXXV). These [illegible] were effected with [illegible] [illegible].

4. It was [illegible] (XXXV) is formed in the presence of [illegible].

5. The [illegible] of [illegible] and it was observed that the [illegible] (VIII) is formed [illegible].

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THE SULFONATION REACTION

XXXI. THE INITIAL RATIOS OF NAPHTHALENEDISULFONIC ACIDS

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It is known that in the sulfonation of naphthalene to monosulfonic acids, two isomers are always obtained, one of which – depending upon the temperature and the duration of sulfonation – predominates. There are no conflicting statements in the literature about the quantities of isomers formed at high temperatures (130-165°), but the data about the ratios of isomers formed at temperatures of 0 to 60°, i.e. when their isomerization has not yet taken place, are extremely conflicting.

Thus, Fierz-David [1] considers that below 40° 4% β-sulfonic acids and 96% α-acids are formed. According to Lantz [2] at 20 to 60° 11-13% β-sulfonic acids are formed. According to the data of works analyses [3], the content of the β-isomer reaches 15%. At 7 to 80°, Perelman [4] obtained 15-18% β-sulfonic acids.

While not concerning ourselves at all with the problem of the formation of isomeric disulfonic acids, we set forth the literature data on the amounts of isomers which are formed at low temperatures, i.e. when they do not yet undergo isomerization.

Fierz-David and Hasler [5] point out that sulfonation of naphthalene at 40° gives about 25% 1,6-disulfonic acid and 70% 1,5-disulfonic acid. Ufimtsev and Krivoshlykova [6] sulfonated naphthalene-β-sulfonic acid at the ordinary temperature and obtained about 20% 1,7-disulfonic acid and 80% 1,6-disulfonic acid. According to the data of works analyses [8], the ratio of 1,5- to 1,6-isomer resulting from sulfonation of naphthalene at 20-60° is 65:35. At the Dorogomilov plant [9] operation at a sulfonation temperature of 25° gave 71-72% 1,5-disulfonic acid; with a higher sulfonation temperature up to 65°, the amount of 1,5-isomer was found to be 60%. Lantz [10] found that in sulfonation of α-sulfonic acid at low temperatures there is formed 77% 1,5-acid together with an unknown acid (apparently 1,7-disulfonic acid) and 23% 1,6-acid. Sulfonation of β-acid gave 70% 1,6-acid, 16% x-acid (probably 1,7-) and 7% each of 2,6- and 2,7-isomers. However, Lantz made the qualification that the measurements were not carried out with the accuracy needed for quantitative study and that methods of analysis were employed which were only suitable for mixtures containing not more than three disulfonic acids. Fierz-David and Richter [11] also sulfonated the β-acid and found in the sulfonated mixture 20% 1,7-disulfonic acid and 80% 1,6-acid.

The composition of the sulfonated mixture obtained by the action of chlorosulfonic acid on naphthalene has scarcely been studied. Armstrong [12] was of the opinion that only the 1,5-disulfonic acid is obtained. V. M. Rodionov [13] obtained 88% of the theoretical yield of unpurified 1,5-disulfochloride, while Pollak and co-workers [14] obtained 59%. The literature does not mention whether and in what quantities other isomers are formed by the action of chlorosulfonic acid upon naphthalene.

In this investigation, we undertook to establish the content of α- and β-isomers obtained by monosulfonation of naphthalene and then, after sulfonating the α- and β-sulfonic acids, to determine the amounts of disulfonic acids formed and to calculate the initial ratios of disulfonic isomers which are formed on sulfonation of naphthalene in conditions in which isomerization has not yet taken place.

EXPERIMENTAL

Monosulfonation of naphthalene was performed at temperatures of 0 and 57°, i.e. below the temperature (70°) at which the α-acid begins to hydrolyze [15]. The reaction was carried out in a hermetically closed broad test tube fitted with a tube and a ground-glass stopper into which was fused a narrow tube. Attached to the latter was a rubber tube through which passed a stirrer tightly fitting into the rubber tube.

To a weighed amount of naphthalene with cooling and stirring, sulfuric acid was added, dropwise, through the tube in the course of ten minutes, and the mixture was then stirred for 10 hours. After solution in water, the unreacted naphthalene was separated and determined by the method previously described by one of us [15]. The total acidity of the filtrate was determined; from the amount of residual naphthalene, the sulfuric acid taken, and the total acidity, the amount of monosulfonic acids in the mixture was calculated. The discrepancies in the amount of monosulfonic acids found on the basis of the naphthalene and on the basis of the change of acidity fluctuated within the range of 0.2.-1% and demonstrated the absence of disulfonic acids. The content of α-acid was determined by precipitation with m-nitro-o-anisidine [16].

The experimental results, set forth in Table 1, showed that 85% of α-isomer is obtained regardless of whether the sulfonation is performed at 0 or 57°.

TABLE 1

Sulfonation of Naphthalene with 99.8 % Sulfuric Acid over a Period of 10 hours

Expt. No.	Moles H_2SO_4 taken per mole naphthalene	Temp. (°C)	Found	
			Conc. of sulfuric acid in mixture (%)	α-acid in % of sum of monosulfonic acids (%)
270	2.071	0-1	94.2	85.0
271	2.003	0-1	93.5	85.3
272	2.044	56-57	89.2	85.5
274	1.701	56-57	86.8	85.2

Sulfonation of α-naphthalenesulfonic acid. A weighed amount of the dihydrate of the α-acid was dried in the same vessel in vacuum over phosphorus pentoxide at 76-78° until nearly the whole of the water was lost; then, with cooling and stirring, oleum was added from a dropping funnel through the tube. The residues of oleum on the walls of the funnel were washed into another vessel and titrated; the tube was closed and the vessel kept for 12 hours at room temperature and for 5 hours at 56-57° with periodic stirring. The weight of the vessel after the experiment confirmed its hermeticity. A portion of the sulfo mass was then analyzed by the method of exhaustive sulfonation which we previously described [17], while the residual amount was dissolved in a measuring flask for determination of the total acidity and the content of 1,5-isomer by the benzidine and xylidine method [18].

The experimental results, set forth in Table 2, showed that sulfonation of the α-acid gives (in round figures): 75% 1,5-disulfonic acid, 10% 1,6-disulfonic acid, 15% 1,3- and 1,7-disulfonic acids.

The formation of 1,7-disulfonic acid on sulfonation of the α-acid had not previously been reported. The amount of 1,3-isomer is considerably less than the amount of 1,7-isomer.

TABLE 2

Sulfonation of α-Naphthalenesulfonic Acid at 56-57° in the Course of 5 hours with 20.4% Oleum

Expt. No.	Moles free SO_3 taken per mole α-acid	Found (in % of sum of sulfonic acids)					Remarks
		α-acid	1,5-acid by benzidine method	1,5-acid by xylidine method	1,6-acid	1,3- and 1,7-acids	
282	0.775	0.3	74.3	74.1	9.4	16.1	We assume that the α-acid is transformed by exhaustive sulfonation into tetrasulfonic acid
284	0.801	1.3	73.3	75.1	10.1	14.4	
291	0.789	0.9	72.3	74.2	9.8	16.0	

Sulfonation of β-naphthalenesulfonic acid was carried out by the same procedure as for the sulfonation of the α-acid, except that the oleum was introduced in such quantity that the free sulfur trioxide was only sufficient for binding the water of crystallization of the sufonic acid (1 mole). The sulfo mixture was analyzed by the indicated methods [17, 18]. In the sulfonation of β-acid, the formation is possible of α,β- and β,β-isomers, while formation of 1,5-acid is impossible. In the determination of 2,7-acid in the form of benzidinesulfonate the 1,6-isomer was isolated as well as the 2,7-isomer. This prompted us to double the dilution of the solutions in comparison with the previous instructions and led to a very large correction for the loss of 2,7-isomer.

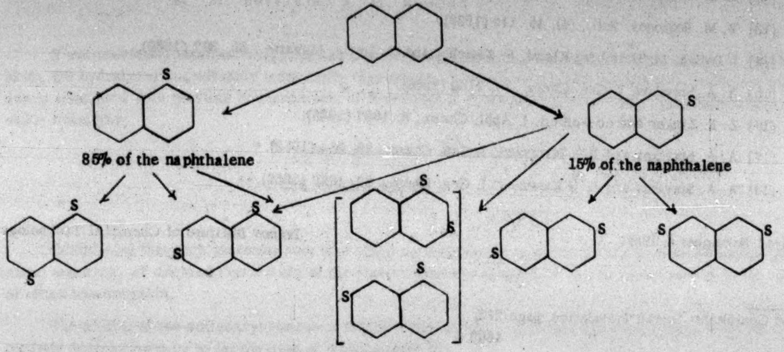
The results of the experiments, set forth in Table 3, showed that sulfonation of the β-acid gives (in round figures): 67% 1,6-disulfonic acid, 21% 1,3- and 1,7-disulfonic acids, 11% 2,7-disulfonic acid and 1% 2,6-disulfonic acid.

TABLE 3

Sulfonation of β-Naphthalenesulfonic Acid at 56-57° in the Course of 5 hours with 99.5% Sulfuric Acid

Expt. No.	Moles H_2SO_4 taken per mole β-acid	Found (in % of total sulfonic acids)					Remarks
		Trisulfonic acids	2,6-acid	2,7-acid	1,6-acid	1,3-and 1,7-acids	
290	4.833	1.2	1.1	12.4	63.8	21.5	We assume that exhaustive sulfonation of the trisulfonic acids gives 50% tetrasulfonic acids.
292	5.838	3.6	1.2	10.3	65.7	19.2	

The data for the composition of the sulfonic acid mixtures obtained on sulfonation of the α- and β-acids permits calculation of the composition of the disulfonic mixtures obtained by direct sulfonation of naphthalene and in the absence of isomerization. The disulfonic mixture obtained by sulfonation of naphthalene contains: 64% 1,5-disulfonic acid, 18% 1,6-disulfonic acid, 16% 1,3- and 1,7-disulfonic acids, 1.7% 2,7-disulfonic acid, 0.2% 2,6-disulfonic acid (see scheme)*



75% of α-isomer	10% of α-isomer	15% of α-isomer	0% of α-isomer	0% of α-isomer
0% of β-isomer	67% of β-isomer	21% of β-isomer	1% of β-isomer	11% of β-isomer
63.7% of naphthalene	18.5% of naphthalene	16.3% of naphthalene	0.2% of naphthalene	1.7% of naphthalene

The experiments on the sulfonation of naphthalene and its monosulfonic acids consequently show that the isomer most labile toward hydrolysis is formed predominantly. Thus from naphthalene we get mainly α-acid; from α-acid mainly 1,5-disulfonic acid; from β-acid 1,6-disulfonic acid. This rule can also be extended to β,β-isomers from which always more of the more labile 2,7-isomer than of the 2,6-isomer appears in the sulfonic mixture; in conditions of absence of their hydrolysis the ratio of 2,6- to 2,7-isomer is 1:8.5.

SUMMARY

The ratio of α- and β-naphthalenesulfonic acids formed by sulfonation of naphthalene at low temperatures was determined. Sulfonation of α- and β-sulfonic acid at low temperature (57°) was followed by determination of the amount of sulfonic acids formed in each case.

The composition was calculated of the disulfonic acid mixture obtained on direct sulfonation of naphthalene in conditions of absence of isomerization.

It is shown that the isomers which are the most labile of all to hydrolysis are formed in preponderance.

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*S denotes SO_3H.

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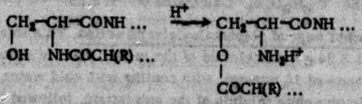
* See Consultants Bureau Translation, page 265.

** " " " " " 1663.

SYNTHESIS OF DERIVATIVES OF SERINE PEPTIDES

M. M. Botvinik, S. M. Avaeva and E. A. Mistryukov

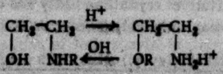
It was previously established [1] that the peptide bonds in protein, formed at the amino group of β-hydroxamino acids, are hydrolyzed considerably more easily than others. It was shown (indirectly) that this phenomenon is evidently associated with previous rearrangement of N-peptides of β-hydroxamino acids into O-peptides, which then easily hydrolyze.



$$\underset{\displaystyle OH}{CH_2}-\underset{\displaystyle NHCOCH(R)\ldots}{CH}-CONH\ldots \xrightarrow{H^+} \underset{\underset{\displaystyle COCH(R)\ldots}{\displaystyle O}}{CH_2}-\underset{\displaystyle NH_2H^+}{CH}-CONH\ldots$$

Considering that such processes may take place not only during acidic hydrolysis of proteins but also in the animal organism, we decided that a study of the phenomenon of migration of the aminoacyl residue in the peptides of serine was desirable.

The ability of the aminoacyl residue to migrate from nitrogen to oxygen and from oxygen to nitrogen was recently demonstrated by us for the case of ethanolamine [2]

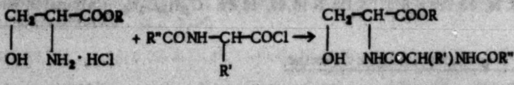


$$\underset{\displaystyle OH}{CH_2}-\underset{\displaystyle NHR}{CH_2} \underset{OH}{\overset{H^+}{\rightleftarrows}} \underset{\displaystyle OR}{CH_2}-\underset{\displaystyle NH_2H^+}{CH_2}$$

where R = $COCH_2NHCOC_6H_5$, $COCH(CH_2C_6H_5)NHCOC_6H_5$, $COCH_2NHCOCH_2NHCOC_6H_5$.

For the purpose of studying this phenomenon with derivatives of β-hydroxamino acids, a series of esters, amides and acylated peptides of serine were synthesized.

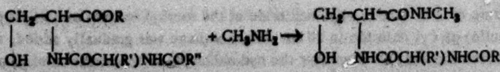
The synthesis was effected by reaction between hydrochlorides of serine esters and chlorides of acylated amino acids in conditions slightly departing from those given in the literature. Experiments were performed in presence of tertiary amines, which greatly simplified the course of the reaction and improved the yield of peptides [3].



$$\underset{\displaystyle OH}{CH_2}-\underset{\displaystyle NH_2\cdot HCl}{CH}-COOR + R''CONH-\underset{\displaystyle R'}{CH}-COCl \rightarrow \underset{\displaystyle OH}{CH_2}-\underset{\displaystyle NHCOCH(R')NHCOR''}{CH}-COOR$$

The following were synthesized: isopropyl ester of N-(phthaloylglycyl)-serine in 72% yield; methyl ester of N-(phthaloylglycyl)-serine in 54% yield; methyl ester of N-(benzoylphenylalanyl)-serine in 71% yield. The last-named was obtained in the form of two diastereoisomers.

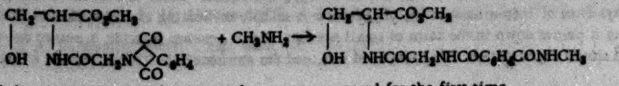
In presence of methylamine, the methyl esters were transformed into the corresponding amides of N-acyl derivatives of peptides of serine



$$\underset{\displaystyle OH}{CH_2}-\underset{\displaystyle NHCOCH(R')NHCOR''}{CH}-COOR + CH_3NH_2 \rightarrow \underset{\displaystyle OH}{CH_2}-\underset{\displaystyle NHCOCH(R')NHCOR''}{CH}-CONHCH_3$$

The following were synthesized: methylamide of N-(p-toluenesulfoglycyl)-serine in 75% yield and the methylamide of N-(benzoylphenylalanyl)-serine in about 100% yield.

In the reaction of the methyl ester of N-(phthaloylglycyl)-serine with methylamine, the dimethylamide of N-phthaloylglycylserine was isolated instead of the anticipated amide



All the above-mentioned compounds are now prepared for the first time.

EXPERIMENTAL

1. Preparation of isopropyl ester of N-(phthaloylglycyl)-serine. To a solution of 1.12 g phthaloylglycyl chloride in 5 ml dioxane was added 0.92 g of the hydrochloride of the isopropyl ester of serine and (gradually) 2 ml diethylaniline (the solution being cooled from time to time). Mixing resulted in rapid solution with appreciable heat generation. Crystals rapidly separated and after 20-25 minutes the reaction mixture was very viscous. After an interval of 50 minutes from the start of the reaction, addition was made of 15 ml ligroine. The reaction mixture formed two layers which after energetic shaking for an hour changed into a thick, crystalline mass. After filtration and washing on the filter first with ligroine and then with water, the substance was recrystallized from chloroform (a mixture of dichloroethane and ligroine could also be used) to give 1.27 g isopropyl ester of N-(phthaloylglycyl)-serine. Yield 72%, m.p. 187°.

Found %: N 8.58, 8.56. $C_{16}H_{18}O_6N_2$. Calculated %: N 8.38.

2. Preparation of methyl ester of N-(phthaloylglycyl)-serine. To a solution of 8.94 g phthaloylglycyl chloride in 20 ml dioxane was added 8.24 g hydrochloride of the methyl ester of serine (m.p. 134°). To the resultant suspension was added in the course of 10 minutes, with cooling with cold water, 12 g diethylaniline dissolved in 10 ml dioxane. This caused nearly complete solution of the precipitate, followed after 15 minutes by separation of the methyl ester of N-(phthaloylglycyl)-serine. After an hour the reaction mass solidified. The dioxane was driven off in vacuum, the residue worked up with water, filtered and recrystallized from alcohol.

Yield 6.7 g methyl ester of N-(phthaloylglycyl)-serine or 54% of the theoretical.

Found %: N 9.20. $C_{14}H_{14}O_6N_2$. Calculated %: N 9.15.

Since the esters of the serine derivatives crystallize badly and are, therefore, difficult to purify, the prepared compounds were utilized in the subsequent ammonolysis reaction without further purification or further investigation.

Reaction of methyl ester of N-(phthaloylgycyl)-serine with methylamine. To 1.08 g methyl ester of N-(phthaloylglycyl)-serine was added 5 ml of 33% solution of methylamine in methyl alcohol, rapid solution being observed. The reaction mass was kept at room temperature for 48 hours. A small quantity of crystals came down and was redissolved by gentle heating. The excess of methylamine and methyl alcohol was driven off in vacuum and the residual crystalline mass dissolved in alcohol. Addition of ether to the alcoholic solution brought down 0.95g substance with m.p. 160°, readily soluble in water and alcohol, insoluble in ether and acetone.

Judging by the analysis the prepared compound was the dimethylamide of phthaloylglycylserine.

Found %: C 53.74, 53.72; H 6.07, 6.13; N 16.93, 16.89. $C_{15}H_{20}O_5N_4$. Calculated %: C 53.57; H 5.95; N 16.66.

Methyl ester of N-(p-toluenesulfoglycyl)-serine.

a) 4.7 g N-(p-toluenesulfo)-glycine (m.p. 145-146°), 4.5 g phosphorus pentachloride and 20 ml dichloroethane were stirred for an hour at room temperature; much hydrogen chloride was evolved. After complete solution, addition was made to the reaction mixture of 20 ml toluene. A gelatinous precipitate came down and was filtered. The filtrate was evaporated in vacuum at 30° and the precipitate was triturated with ligroine and transferred to a filter. It was N-(p-toluenesulfo)-glycyl chloride. Yield 3.2 g (63.0%). M.p. 85°. The substance was used without further purification.

b) To a mixture of 2.02 g of the hydrochloride of the methyl ester of serine (m.p. 134°) and a solution of 3.2 g N-(p-toluenesulfo)-glycyl chloride in 20 ml dichloroethane was gradually added, with stirring, 6 ml diethylaniline. With considerable heat development the hydrochloride of the serine methyl ester dissolved. After standing for an hour at room temperature, the whole mass thickened up considerably, owing to separation of crystals. 20 ml ligroine and 25 ml water were added; two transparent layers were formed. Shaking for an hour led to crystallization. The crystals were filtered, washed with ether and dissolved in butyl alcohol by heating. The insoluble portion was rejected and the filtrate was worked up with ether. The resultant crystals were filtered and washed with ether.

There was obtained 2 g methyl ester of N-(p-toluenesulfoglycyl)-serine. Yield 46% of the theoretical, m.p. 148-149°. The methyl ester of N-(p-toluenesulfoglycyl)-serine is soluble on heating in ethyl alcohol, dichloroethane and water; on cooling it comes down in the form of small needles. From aqueous solution it comes down in the form of an oil which slowly crystallizes. The compound was used for ammonolysis without further examination or purification.

Found %: N 8.49, 8.51, $C_{13}H_{18}O_6N_2S$. Calculated %: N 8.48.

Methylamide of N-(p-toluenesulfoglycyl)-serine. To 2 g methyl ester of N-(p-toluenesulfoglycyl)-serine was added 20 ml of 33% solution of methylamine in methyl alcohol. After 48 hours at room temperature, the methyl alcohol and the methylamine were distilled off in vacuum. The oily residue crystallized when triturated with a mixture of acetone and ether (1:1). The methylamide of N-(p-toluenesulfoglycyl)-serine was recrystallized from water. Yield 1.5 g (75%), m.p. 145°. It crystallizes from water in tablets. Soluble in methyl and ethyl alcohols, insoluble in ether.

Found %: C 47.68, 47.93; H 5.92, 6.01; N 12.8, 12.9; S 10.40, 10.35. $C_{13}H_{19}O_5N_3S$. Calculated %: C 47.41; H 5.77; N 12.76; S 9.72.

Methyl ester of N-(benzoylphenylalanyl)-serine. 2-Phenyl-4-benzyl-5-oxazolone, prepared by Mohr's method from 5.4 g benzoylphenylalanine, was dissolved in 15 ml dichloroethane and the resultant solution was gradually added to a solution of 3.12 g hydrochloride of serine methyl ester and 3.46 ml dimethylbutylamine in 15 ml dichloroethane. The reaction mixture was stirred for an hour. Solution was complete after 30 minutes. The solution was shaken with 20 ml water, then with 10 ml N-hydrochloric acid and again with 10 ml water. After drying over sodium sulfate, the dichloroethane was driven off in vacuum. The residue was a thick, resinous mass which was dissolved in alcohol and treated with 10 ml water. On shaking the heterogeneous mixture and cooling to 0°, crystals came down. These were filtered and washed 3 times with ether. There was obtained 3.2 g methyl ester of N-(benzoylphenylalanyl)-serine (preparation A). Yield 43% of the theoretical. M.p. 158-159°.

Found %: C 65.48, 65.51; H 6.18, 6.27; N 7.52, 7.66. $C_{20}H_{22}O_5N_2$. Calculated %: C 64.85; H 5.90; N 7.56.

From the mother liquor remaining after separation of the methyl ester of N-(benzoylphenylalanyl)-serine was obtained yet another substance (preparation B) by treatment with ligroine. Yield 28% of the theoretical. M.p. 138-140° (from benzene). A mixed test with the methyl ester of N-(benzoylphenylalanyl)-serine (A) gives a m.p. depression of 15°. The compound was evidently the diastereoisomer of preparation A, since on treatment with methylamine it is transformed into the methylamide of N-(benzoylphenylalanyl)-serine.

Methylamide of N-(benzoylphenylalanyl)-serine.

a) From methyl ester of N-(benzoylphenylalanyl)-serine with m.p. 158-159°. To 2 g methyl ester of N-(benzoylphenylalanyl)-serine was added a tenfold excess of 33% solution of methylamine in methyl alcohol, and the solution was left 24 hours at room temperature. Part of the formed methylamide crystallized out. After inspissation of the mother liquor, the remainder separated.

On recrystallization from 50% aqueous alcohol, the methylamide of N-(benzoylphenylalanyl)-serine separates in the form of lustrous tablets soluble in hot ethyl and butyl alcohols and sparingly soluble in hot water. Yield of methylamide (A') nearly quantitative. M.p. 210°.

Found %: C 65.39, 65.35; H 6.38, 6.38; N 11.39, 11.40. $C_{20}H_{23}O_4N_3$. Calculated %: C 65.04; H 6.24; N 11.38.

b) From methyl ester of N-(benzoylphenylalanyl)-serine with m.p. 138-140°. The mother liquor remaining after separation of the methyl ester with m.p. 158-159° (A) was used for preparation of the amide. Evaporation of the mother liquor in vacuum left a viscous oil which was worked up with a tenfold excess of 33% solution of methylamine in methyl alcohol in which the oil dissolved completely. After 24 hours, the reaction mass set, owing to separation of crystals. These were filtered and recrystallized from a mixture of ethyl alcohol and acetic acid. The methylamide of N-(benzoylphenylalanyl)-serine (preparation B') forms acicular crystals. M.p. 230°.

Found %: C 65.43, 65.28; H 6.44, 6.42; N 11.4, 11.0. $C_{20}H_{23}O_4N_3$. Calculated %: C 65.04; H 6.24; N 11.38.

SUMMARY

The synthesis of a series of derivatives of serine peptides is described.

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FURAN COMPOUNDS

V. PREPARATION AND PROPERTIES OF 3-(2'-METHYL-5'-FURYL)-PROPEN-2-AL AND SOME OTHER DERIVATIVES OF 5-METHYL-2-FURALDEHYDE

A. A. Ponomarev and M. D. Lipanova

The condensation of 2-furaldehyde with various aldehydes and ketones has been the subject of numerous investigations. This route has served, in particular, for the synthesis of many unsaturated furanic aldehydes: furylacrolein its homologs, furylpentadienal, etc.; these investigations have been adequately reviewed in a series of papers [1, 2]. Of the unsaturated aldehydes of the furan series the most accessible and the one of greatest practical importance was furylacrolein, whose preparation and properties have been studied by many authors. M. V. Likhosherstov and co-workers [1] developed a novel method of synthesis of furylacrolein in a yield of up to 85%. These authors also closely investigated the reduction of furylacrolein with aluminum ethylate and established that in certain conditions the yield of furylallyl alcohol may reach 60-70%.

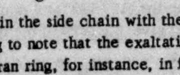
5-Methyl-2-furaldehyde has received very much less attention from investigators than 2-furaldehyde. This is also true in respect of such simple derivatives as unsaturated aldehydes and ketones. In the present paper we report the preparation and properties of some new derivatives of 5-methyl-2-furaldehyde. We have already [3, 4] described the synthesis of 3-(2'-methyl-5'-furyl)-propen-2-al from 5-methyl-2-furaldehyde and acetaldehyde. For its preparation we utilized at the time conditions similar to those adopted by M. V. Likhosherstov [1] for the synthesis of furylacrolein, i.e. condensation was effected with gradual addition of the acetaldehyde to a mixture, cooled to 0°, of 5-methyl-2-furaldehyde and a 0.5% solution of sodium hydroxide. The yield of 3-(2'-methyl-5-furyl)-propen-2-al was only 28% of the theoretical. Repeated experiments with maintenance of the specified conditions gave the same results.

In a further systematic study of this reaction it has been found that 3-(2'-methyl-5'-furyl)-propen-2-al is formed in considerably more satisfactory yield (67% of the theoretical) if the method is slightly modified so that the acetaldehyde (in slight excess) is added gradually to a mixture, kept at 20°, of 5-methyl-2-furaldehyde and 10% aqueous NaOH.

The 3-(2'-methyl-5'-furyl)-propen-2-al was further converted (in a yield of 27% of the theoretical) into 3-(2'-methyl-5'-furyl)-propen-2-ol-1 (methylfurylallyl alcohol) by reduction with aluminum ethylate in conditions similar to those for the preparation of furylallyl alcohol from furylacrolein [1]. The acetate of 3-(2'-methyl-5'-furyl)-propen-2-ol was also prepared.

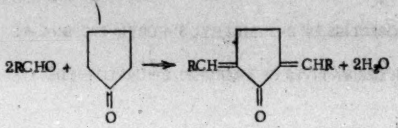
It is a matter of some interest to compare the physical properties of furylacrolein and furylallyl alcohol and their methyl homologs.

In Table 1 are set forth the data for all the above-mentioned substances.

We see from this table that furylacrolein and its methyl homologs are characterized by a EM_D of the order of 5 units, which is in full accord with the observation by a number of other authors [5, 6] of a considerable exaltation (4.1 to 5.8) in the case of furfurylidene ketones of the type of 

A similar phenomenon also occurs in other cases of conjugation of the double bond in the side chain with the furan ring and carbonyl (e.g. ethyl furylacrylate [7] has EM_D + 4.481); it is interesting to note that the exaltation is much lower when only a double bond in the side chain is conjugated with the furan ring, for instance, in furylethylene [7] EM_D 1.63, i.e., nearly the same as in 2-furaldehyde (1.61). As would also be expected in the light of the foregoing remarks, the molecular exaltations of furylallyl alcohols proved to be considerably lower than those of the corresponding alcohols; in absolute magnitude they are close to the exaltation of furylethylene.

In Table 2 are set forth the data for some physical properties and color reactions of furanic unsaturated ketones which we prepared by condensation of 5-methyl-2-furaldehyde and 3-(2'-methyl-5'-furyl)-propen-2-al with cyclopentanone and cyclohexanone:



All such ketones possess a symmetrical structure and are formed in accordance with the above scheme.

The close similarity between the above-enumerated ketones and the corresponding derivatives of 2-furaldehyde and furylacrolein is noteworthy.

EXPERIMENTAL

5-Methyl-2-furaldehyde was prepared from saccharose [11] as an oily liquid with b.p. 75-76° at 12 mm. Yield 22%.

Found %: C 65.81; H 5.93. $C_6H_6O_2$. Calculated %: C 65.45; H 5.50.

3-(2'-Methyl-5'-furyl)-propen-2-al. 450 ml 10% aqueous sodium hydroxide is mixed with 50 g 5-methyl-2-furaldehyde and a solution of 30 g acetaldehyde in 150 ml water is slowly stirred in at room temperature over a period of 2 1/2 hours. After all has been added, the mixture is stirred for another hour. The light-brown oil which separates at the bottom of the flask is collected; the aqueous layer is neutralized with 80% acetic acid and extracted 3 times with ether. The ethereal extracts are added to the oil and the ethereal solution is dried with calcined sodium sulfate. The ether is driven off and the residue distilled in vacuum at 5 mm. A fraction with b.p. 98-130° is collected and subjected to a second distillation. Methylfurylacrolein comes over at 100-102° (5 mm). Yield 41.5 g (67.13% of theoretical).

n_D^{20} 1.6089; d_4^{20} 1.1006; MR_D 42.82; Calc. 37.197.

Found %: C 70.53; 70.19; H 5.99, 5.69; M 134.1. $C_8H_8O_2$. Calculated %: C 70.57; H 5.92; M 136.14.

3-(2'-Methyl-5'-furyl)-propen-2-al is a yellow oil with an odor resembling that of furylacrolein but less pungent; it has a sweet taste; it is soluble in the common organic solvents, slightly soluble in water; darkens on keeping.

The semicarbazone is prepared by mixing an alcoholic solution of the aldehyde with a solution of semicarbazide hydrochloride and sodium acetate and directly heating the reaction mixture. Forms beautiful white scales. The yield is quantitative. M.p. 191° (after 3 recrystallizations from alcohol).

Found %: N 21.51, 21.35; $C_9H_{11}O_2N_3$. Calculated %: N 21.74.

The dinitrophenylhydrazone, prepared by the usual method, forms red crystals with m.p. 216-216.5° (after 3 recrystallizations from a mixture of alcohol and ethyl acetate).

3-(2'-Methyl-5'-furyl)-propen-2-ol-1. Into a round-bottomed flask, fitted with a Hahn column, were introduced 30 g 3-(2'-methyl-5'-furyl)-propen-2-al, 150 ml dry benzene and 27 g aluminum ethylate; heating was carried out on a water bath until the benzene boiled, while passing a weak stream of nitrogen. The experiment lasted 2 1/2 hours. At the end of the experiment the solution had darkened appreciably. The benzene solution was then run in small portions into cooled 10% sulfuric acid whose amount was calculated for complete binding of the aluminum (245 ml). The benzene solution was separated and the aqueous portion further extracted with two portions (50 ml) benzene. The combined benzene extracts were washed with a small quantity of sodium carbonate solution and then with water and dried with calcined sodium sulfate. After driving off the solvent, the residue was distilled in vacuum and a first broad fraction (120-140° at 6 mm) collected. A second distillation of this fraction in vacuum (from a flask with a column) gave 8 g (27% of the theoretical) of 3-(2'-methyl-5'-furyl)-propen-2-ol with b.p. 125° (15 mm).

n_D^{20} 1.5561; d_4^{20} 1.088; MR_D 40.83; Calc. 38.71.

Found %: C 69.61, 69.81; H 6.85, 6.86; OH 10.55, 10.51. $C_8H_{10}O_2$. Calculated %: C 69.54; H 7.29; OH 12.3 %.

TABLE 1

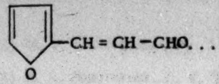
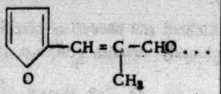
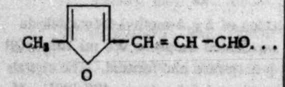
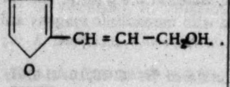
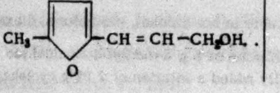
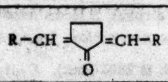
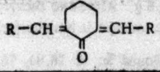
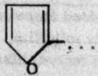
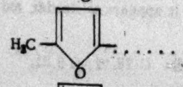
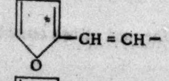
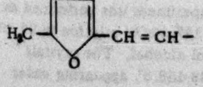
Structural formula	B.p. (°C)	d_4^t	n_D^t	MR_D found	MR_D calculated	M.p. of semicarbazone	Literature
	97 (10 mm)	1.1163 (at m.p.)	1.617 (at m.p.)	38.28	~~32.579~~	219	[5, 12]
	100 (11 mm)	1.1022 (13.5°)	1.613 (13.5°)	42.99	37.197	250.5-251.5	[5]
	100-102 (5 mm)	1.1066 (20°)	1.6089 (20°)	42.82	37.197	191	–
	123-124 (20 mm)	1.1001 (17.5°)	1.5514 (17.5°)	35.98	34.09	–	[1]
	125 (15 mm)	1.088 (20°)	1.5561 (20°)	40.83	38.71	–	–

TABLE 2

R								
	Color	M.p. (°C)	Color reactions*		Color	M.p. (°C)	Color reactions*	
			Conc. H_2SO_4	$SbCl_3$ and $CHCl_3$			Conc. H_2SO_4	$SbCl_3$ and $CHCl_3$
	Yellow	162-163 [8]	Dark-blue	Yellow, changing to green	Lemon-yellow	145 [9]	Violet	Yellow changing to green
	Yellow	131-132	Dark-blue	Green, changing to blue	Lemon-yellow	118-119	Violet	Green, changing to dark-blue
	Orange	151-152 [10]	Blue-green	Blue	Yellowish orange	162.4 [10]	Bluish-green	Blue
	Cherry red	165-166	Blue-green	Blue	Orange	168-168.5 [4]	Bluish-green	Blue

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*The color developed on adding particles of the substance to concentrated sulfuric acid, or on putting on filter paper drops of 1% solution of $SbCl_3$ in chloroform containing a particle of the substance.

The alcohol is a yellowish oil with a pleasant odor, soluble in the common organic solvents, slightly soluble in water. It polymerizes relatively quickly when kept.

The acetate is prepared by heating a mixture of 4.4 g acetic anhydride, 1 g fused sodium acetate and 4 g methylfurylallyl alcohol for an hour on a water bath. The reaction mixture is washed with water, then with sodium carbonate solution, and extracted with ether. The extract is dried with calcined sodium sulfate, the ether is driven off and the residual oil distilled in vacuum. A fraction (1.28 g) with b.p. 107-109° (5 mm) is collected. Greenish-yellow liquid with a pleasant odor.

n_D^{20} 1.5221; d_4^{20} 1.0736; MR_D 51.2; Calc. 48.07.

Found %: C 66.72; H 6.80. $C_{10}H_{12}O_3$. Calculated %: C 66.65; H 6.71.

The phenylurethane was prepared by mixing equimolar amounts of the alcohol and phenylisocyanate and heating the mixture. White crystals. After 3 recrystallizations from carbon tetrachloride, needles with m.p. 106°.

Found %: N 5.7. $C_{15}H_{15}NO_3$. Calculated %: N 5.57.

Condensation of 5-methyl-2-furaldehyde with cyclopentanone. To a solution of 5 g 5-methyl-2-furaldehyde (0.0454 mole) and 1.9 g cyclopentanone (0.0227 mole) in 20 ml 60% alcohol was added dropwise 0.5 ml 10% NaOH solution. Heat was developed and after a short interval, a voluminous orange precipitate had formed. The crystals were separated and washed with water and dilute alcohol. Yield of unpurified material 5.6 g (m.p. 128-129°). After two recrystallizations from alcohol, yellow acicular crystals were obtained with monoclinic syngony and slight pleochroism. M.p. 131-132°.

Found %: C 75.94, 76.36; H 6.47, 5.86; M 250.4 (Rast). $C_{17}H_{16}O_3$. Calculated %: C 76.10; H 6.01; M 268.29.

The ketone is poorly soluble in cold alcohol and benzene; readily soluble in hot alcohol, chloroform, dioxane..

Condensation of 5-methyl-2-furaldehyde with cyclohexanone. To a solution of 5 g 5-methyl-2-furaldehyde (0.0454 mole) and 1 ml 10% NaOH solution in 20 ml 60% alcohol is gradually added a solution of 2.22 g cyclohexanone (0.0227 mole) in 5 ml alcohol. Heat is developed and the mixture turns cloudy; after a short interval a crystalline precipitate appears. This is collected and washed with water and dilute acetic acid. Weight of unpurified product 6.5 g. After two recrystallizations from alcohol, it forms lemon-yellow needles with m.p. 118-119°. Under the microscope it has the form of elongated, canary-yellow, hexagonal prisms which are strongly pleochroic.

Found %: C 76.84, 76.39; H 6.55, 6.69; M 280.1 (Rast). $C_{18}H_{18}O_3$. Calculated %: C 76.57; H 6.43; M 282.3.

The ketone is insoluble in cold and hot water, sparingly soluble in cold alcohol and benzene; it is readily soluble in hot alcohol, chloroform and dioxane.

Condensation of 3-(2'-methyl-5'-furyl)-propen-2-al with cyclopentanone. To a solution of 2 g methylfurylacrolein (0.014 mole) and 0.61 g cyclopentanone (0.07 mole) in 10 ml 60% ethyl alcohol is added dropwise, with shaking, 0.5 ml 10% NaOH solution. After a few minutes a dark oil begins to form and quickly solidifies. The crystals are collected and worked up as previously. Yield of unpurified product, 2.35 g. After recrystallization from isopropyl alcohol, it forms cherry-red needles with m.p. 165-166°. Under the microscope it appears as slender, red prisms without pleochroism and with tetragonal syngony.

Found %: C 78.59, 78.86; H 6.84, 6.82; M 330.57, 329.51. $C_{21}H_{20}O_3$. Calculated %: C 78.72; H 6.31; M 320.37.

The ketone is insoluble in water, poorly soluble in cold alcohol, benzene, gasoline, and carbon tetrachloride; readily soluble in hot alcohol, benzene, chloroform.

Condensation of 3-(2'-methyl-5'-furyl)-propen-2-al with cyclohexanone. The experiment was performed as previously described [4]. To a solution of 6 g of the aldehyde (0.044 mole) and 1 ml 10% NaOH solution in 20 ml 60% alcohol is added dropwise a solution of 2.16 g cyclohexanone (0.022 mole) in 5 ml alcohol. The crystals formed are treated as before. The ketone $C_{21}H_{22}O_3$ forms orange crystals with m.p. 168-168.5°, appearing under the microscope as prismatic tablets, slightly pleochroic from light-orange to deep orange, and possibly possessing rhombic syngony. Insoluble in cold and hot water, poorly soluble in cold alcohol and benzene; readily soluble in hot alcohol, chloroform, dioxane.

SUMMARY

1. A method is developed for the preparation of 3-(2'-methyl-5'-furyl)-propen-2-al which permits the synthesis of this aldehyde in a yield up to 70%. It is shown that 3-(2'-methyl-5'-furyl)-propen-2-al can be reduced with

aluminum ethylate to give the unsaturated alcohol 3-(2'-methyl-5'-furyl)-propen-2-ol-1; the properties of the latter and some of its derivatives are described.

2. A description is given of some properties of unsaturated furanic ketones prepared by condensation of 5-methyl-2-furaldehyde and 3-(2'-methyl-5'-furyl)-propen-2-al with cyclopentanone and cyclohexanone.

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* See Consultants Bureau Translation, page 663.

** See Consultants Bureau Translation, page 1127.

*** See Consultants Bureau Translation, page 1493.

[illegible] and some of its derivatives are described.

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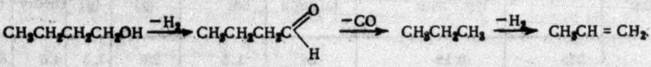
PREPARATION OF THIOPHENE AND ITS HOMOLOGS FROM ALCOHOLS

Yu. K. Yuryev and L. I. Khmelnitsky

According to the data of Conary and co-workers, thiophene and its homologs can be obtained by interaction of hydrocarbons with sulfur dioxide in presence of chromia-on-alumina (20% chromia) at 500-600° [1, 2, 3]. This reaction is applicable to hydrocarbons containing not less than four carbon atoms in a straight chain. Butane and butenes give thiophene in 32% yield (on the hydrocarbon used); hydrocarbons with five and six carbon atoms give the corresponding thiophene homologs in much lower yields, the reaction being complicated by processes of cleavage giving rise to lower homologs of thiophene and thiophene itself.

In this investigation we have studied the interaction of aliphatic alcohols (n-butyl, isoamyl and n-hexyl) with sulfur dioxide in presence of chromia-on-alumina (20% chromia). It was found that the unsaturated hydrocarbons resulting from dehydration of the alcohols can react with sulfur dioxide to give compounds of the thiophene series, and that the optimum conditions for this reaction are 400-450° and a molar ratio of SO_2 to alcohol of 1.5 : 1.

An examination of the liquid and gaseous products of the reaction of n-butyl alcohol with sulfur dioxide in optimum conditions showed that 8-10% of the alcohol is converted (after dehydration) into thiophene, approximately 8% only undergoes dehydration to 1-butene (isomerizing further to 2-butene and partly dehydrogenating to 1,3-butadiene), and approximately 24% of the alcohol is oxidized to butyraldehyde which breaks down to carbon monoxide and propane; the latter dehydrogenates to propene



$$CH_3CH_2CH_2CH_2OH \xrightarrow{-H_2} CH_3CH_2CH_2C\overset{O}{\underset{H}{\lessdot}} \xrightarrow{-CO} CH_3CH_2CH_3 \xrightarrow{-H_2} CH_3CH = CH_2.$$

The remaining (approximately 60%) n-butyl alcohol undergoes more drastic oxidation with formation of carbon monoxide and a carbonaceous mass deposited as a dense layer on the catalyst. Less than 1% of the alcohol is recovered unchanged.

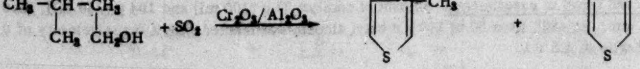
When the n-butyl alcohol is passed over the same catalyst at 450° in the absence of sulfur dioxide, dehydration proceeds normally (to the extent of 95%) with formation of 1-butene which isomerizes to the extent of 80-85% to 2-butene [4] (the percent isomerization was determined by examination of the Raman spectra of the mixture of dibromobutanes formed).

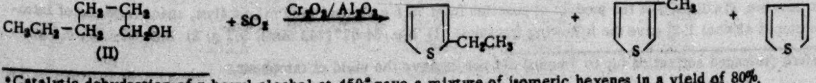
If the alcohol is first dehydrated and then the moist mixture of butenes is brought into reaction with sulfur dioxide at 550°, then thiophene is obtained in 33% yield (calculated on the alcohol).

In the interaction of isoamyl and n-hexyl* alcohols with sulfur dioxide, the formation would be expected of 3-methylthiophene and 1-ethylthiophene or 2,5-dimethylthiophene respectively, or of a mixture of both.

It was found that isoamyl (I) gave, together with 3-methylthiophenol, an insignificant amount of thiophene itself; in the case of n-hexyl alcohol (II), however, the product was 2-ethylthiophene, together with 3-methylthiophene and thiophene, whereas 2,5-dimethylthiophene was not formed at all.

(I)





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*Catalytic dehydration of n-hexyl alcohol at 450° gave a mixture of isomeric hexenes in a yield of 80%.

EXPERIMENTAL

Chromia-on-alumina was prepared by the known method [5]: mixing of a chromic solution with non-calcined aluminum oxide. The catalyst was dried first at 110° and then in a current of air at an elevated temperature up to 450°. The activity of the catalyst was checked by the preparation of thiophene from a mixture of butenes and sulfur dioxide at 550°; the thiophene yield was 25.7% of the theoretical (the literature [1] reports 27.2%). The activity did not diminish after a large number of experiments.

Before each experiment the reaction tube was heated to 550° and the catalyst was activated for 2-3 hours* in an air current after which the operating temperature was established. The sulfur dioxide was passed through a flowmeter, a bubble counter containing sulfuric acid, and entered the reaction tube; the alcohol was run in from a dropping funnel.

1) Thiophene from n-Butyl Alcohol

a) First series of experiments: 35 g (50 ml) catalyst; tube with inner diameter of 13 mm. In each experiment, 25 g (0.34 mole) n-butyl alcohol (b.p. 115-116° at 751 mm; n_D^{20} 1.3981; d_4^{20} 0.8101) was introduced in a stream of sulfur dioxide. Experiments were run at 375, 400, 450, 500 and 550° and SO_2/alcohol molar ratios of 0.6:1 to 3.2:1. The space velocity of the alcohol was varied from 0.1 to 0.5 ml alcohol per ml catalyst per hour.

The reaction tube was connected to two receivers cooled with ice and salt; the main bulk of catalyzate collected in the first receiver. Suspended sulfur hindered the separation of the aqueous layer from the dark, oily layer; the catalyzate was therefore saturated with caustic alkali and extracted with ether. The ethereal extract was dried with fused NaOH and the residue distilled from a flask through a tall and narrow column.

Results of some experiments in this series are set forth in Table 1.

TABLE 1

No. of Experiment	Temperature (°C)	Space velocity of alcohol; ml alcohol/ml catalyst · hour	Velocity of SO_2 ml/min	Molar ratio of SO_2 to alcohol	Wt. of catalyst (g)	Thiophene obtained			Alcohol recovered unchanged		
						(g)	in % theory	b.p. (°C)	(in g)	in % of theory	b.p. (°C)
1	375	0.19	56	1.3	22	1.3	4.6	84-87	1.6	6.4	112-117
6	400	0.10	34	1.5	13	2.5	8.8	84-87	0.35	1.4	113-116
14	450	0.16	56	1.5	16	2.6	9.2	83-86	–	–	–
23	500	0.49	135	1.2	10	0.9	3.2	84-85	–	–	–
26	550	0.44	135	1.4	10	0.75	2.7	83-84	–	–	–

In experiment 14 (Table 1) distillation of the reaction product (obtained at 450°) gave a fraction with b.p. 83-86° (746 mm), 2.6 g (residue 0.2 g) consisting of thiophene (yield 9.2% of the theoretical).

Repeated distillation of the thiophene (24.7 g) from all the experiments over sodium gave pure thiophene (23.5 g): b.p. 83-84° (751 mm); n_D^{20} 1.5250; d_4^{20} 1.0618; MR_D 24.28. $C_4H_4SF_2$. Calculated: MR_D 25.34.

Found %: S 38.10, 38.04. C_4H_4S. Calculated %: S 37.93.

Mercuration [6] of the thiophene gave 2-chloromercurithiophene with m.p. 183-184°.

Found %: Hg 62.91, 62.96. C_4H_3HgCl. Calculated %: Hg 62.85.

Literature data for thiophene [7]: b.p. 84° (760 mm); n_D^{20} 1.5246; d_4^{20} 1.0617; [8]: b.p. 84.12° (760 mm); n_D^{20} 1.5287; d_4^{20} 1.0644. M.p. of 2-chloromercurithiophene [1]: 183-184°.

b) Second series of experiments: amount of catalyst 71 g (100 ml) and 104 g (150 ml), tube with internal diameter 20 mm. At 450°, from 50 to 100 g n-butyl alcohol was reacted with a space velocity of 0.5-1.4 with a SO_2/alcohol ratio of 1.5 : 1.

It was found that the increased space velocity of the alcohol had no effect on the thiophene yield. Thus, for instance, distillation of the product of reaction from 76.5 g alcohol (100 ml catalyst, space velocity of introduction of alcohol 1.3) gave the following fractions: 1) b.p. 84-87° (742 mm), 9.1 g; 2) b.p. 87-112°, 0.3 g;

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* More prolonged activation (up to 7 hours) did not improve the yield of thiophene.

3) b.p. 112-116°, 0.7 g. The first fraction was thiophene (yield 10.5%), the third fraction was unchanged alcohol.

The gaseous products of reaction (79.0 g alcohol, 100 ml catalyst, space velocity of introduction of alcohol 0.72) were purified from hydrogen sulfide, sulfur dioxide, and (partly) carbon dioxide and collected in a gasholder. Gas composition (27 liters at N.T.P.): CO_2 8.1%; CO 20.5%; H_2 36.2%; O_2 2.4%; C_nH_{2n} 20.2%; C_nH_{2n+2} 12.2%.

c) Third series of experiments: into a furnace were introduced two tubes with inner diameter, 16 mm: the first contained 80 g (140 ml) alumina, the second 80 g (115 ml) chromia-on-alumina. Into the first tube, in a weak nitrogen stream, was introduced 71 g alcohol with a space velocity of 0.5, and the mixture of butenes formed was, without drying, passed into the second tube into which was introduced sulfur dioxide at a velocity of 360 ml/min. Molar ratio of SO_2 to alcohol 1.5 : 1. The catalyzate was saturated with alkali and thrice extracted with ether. The ethereal extract was dried with NaOH, the ether was driven off, and the residue distilled to give 26.5 g thiophene which came over at 83-84° (750 mm) (yield 33% calculated on the alcohol brought into the reaction).

d) Reaction between n-butyl alcohol and sulfur dioxide was carried out in presence of alumina alone. Into a tube with an inner diameter of 13 mm was charged 35 g (75 ml) alumina and at 450°, 25 g (0.34 mole) n-butyl alcohol was passed in at a space velocity of 0.3; speed of introduction of sulfur dioxide 100 ml/min. (molar ratio of SO_2 to alcohol 1.5 : 1). The thiophene yield was 1.6 g (5.6% of the theoretical).

2) 3-Methylthiophene from Isoamyl Alcohol

a) First series of experiments: 35 g (50 ml) catalyst; tube with inner diameter of 13 mm. In each experiment was introduced 25.5 g (0.29 mole) isoamyl alcohol [b.p. 128-130° (753 mm); n_D^{20} 1.4060; d_4^{20} 0.8129] in a stream of sulfur dioxide. Experiments were run at 400 and 450°, molar ratio of SO_2 to alcohol of 1.3:1 1.65:1, and space velocity of introduction of alcohol 0.30 to 0.63. The catalyzates were worked up as described above. Yields of 3-methylthiophene at 400 and 450° were substantially identical and reached 12.4%, reckoned on the alcohol used. Thus, for example, distillation of the product of reaction at 400°, molar ratio of SO_2 to alcohol of 1.6:1, and space velocity of introduction of the alcohol 0.30, gave the following fractions: 1) b.p. 84-110° (750 mm), 0.2 g; 2) b.p. 110-113°, 3.3 g; 3) b.p. 113-127°, 0.3 g; 4) b.p. 127-132°, 2.5 g; resinous residue, 0.8 g. The first fraction contained thiophene; the second fraction was 3-methylthiophene (yield 12.4% of theoretical, reckoned on the alcohol used); the fourth was unchanged alcohol.

Redistillation over sodium of the 3-methylthiophene (22 g) from all the experiments gave pure 3-methylthiophene (20.6 g): b.p. 114-115° (751 mm); n_D^{20} 1.5200; d_4^{20} 1.0207; MR_D 29.24. $C_5H_6S\digamma_2$. Calculated MR_D 29.96.

Found %: S 32.62, 32.52. C_5H_6S. Calculated %: S 32.67.

Literature data for 3-methylthiophene [9]: b.p. 115.4° (760 mm); n_D^{20} 1.5204; d_4^{20} 1.0216.

b) Second series of experiments: 100 ml catalyst; tube with inner diameter, 20 mm. In an experiment at 400°, 91 g (1.04 moles) isoamyl alcohol (molar ratio of SO_2 to alcohol of 1.4:1, space velocity of alcohol 0.6) was passed over the catalyst. The catalyzate was worked up with alkali and the oily layer was collected and distilled (to eliminate resin) before drying with fused NaOH; it was then combined with the residue (usually not more than 0.7 g) obtained after driving off the ether (in vacuum) from the ethereal extract of the aqueous layer. Further distillation of the reaction product (from a flask with a tall and narrow column) gave the following fractions: 1) b.p. 83-84° (754 mm), 0.3 g; 2) b.p. 84-112°, 0.4 g; 3) b.p. 112-115°, 8.2 g; 4) b.p. 115-127°, 1.6 g; 5) b.p. 127-130°, 18.4 g; residue 0.8 g. The first fraction was thiophene (yield 0.4% reckoned on the alcohol used), the third was 3-methylthiophene (yield 10%), the fifth was unchanged alcohol (20.2%). In experiments at 450° (other conditions being identical) the yield of thiophene was 8%.

Hence, the increase of space velocity of introduction of the alcohol from 0.3 (first series) to 0.6 (second series) caused a reduction in 3-methylthiophene yield from 12.4 to 10% (at 400°) and to 8% (at 450°).

The corresponding fractions of thiophene from all the experiments of the second series were combined, distilled over sodium and fractionated through a column with an efficiency of 16 theoretical plates, the following fractions being obtained:

	B.p. (747 mm)	n_D^{20}	d_4^{20}	Wt. (in g)
1	70-84°	1.5094	—	0.8
2	84-86	1.5147	1.0326	1.0
3	86-112.5	1.5172	1.0271	3.2
4	112.5-113.5	1.5196	1.0226	4.2
5	113.5	1.5202	1.0217	11.2
6	113.5-119	1.5190	1.0207	1.5

TABLE 2

No. of Experiment	Hexyl alcohol charged (in g)	Space velocity of alcohol charged	Velocity of introduction of SO_2 (ml/min.)	Molar ratio of SO_2 to alcohol	Catalyzate obtained (in g)	B.p. and amount 1 52-84°	2 84-92°	3 92-111°
1	102	0.75	575	1.5	104	19.6	0.8	1 drop
2	91	0.75	575	1.6	92			
3	102	0.34	260	1.5	99	91	0.2	0.1
4	102	0.52	575	2.2	88	5.4	0.4	1 drop

The fifth fraction was pure 3-methylthiophene which was also present in the fourth and fifth fractions.

The second fraction (judging by the boiling point) must be thiophene but the refractive index and density of this fraction were higher than those reported in the literature for thiophene; mercuration [10] was therefore effected of this fraction as well as of the first fraction.

A mixture of 0.6 g first fraction and 0.2 g second fraction gave 1.7 g 2-chloromercurithiophene with m.p. 183-184° (no depression was observed in a mixed test with pure 2-chloromercurithiophene) and 1 g 2,5-di-(chloromercuri)-thiophene; analysis of the latter gave the following results:

Found %: Hg 72.51, 72.59. $C_4H_2SHg_2Cl_2$. Calculated %: Hg 72.38.

Mercuration of 14 g of mixture of the fourth and fifth fractions gave 17.3 g 2-chloromercuri-3-methylthiophene with m.p. 128-129°.

Found %: Hg 60.25, 60.17. C_5H_5SHgCl. Calculated %: Hg 60.20.

There was also obtained 39.1 g 2,5-di-(chloromercuri)-3-methylthiophene.

Found %: Hg 70.34, 70.43. $C_5H_4SHg_2Cl_2$. Calculated %: Hg 70.59.

The literature for 2-chloromercuri-3-methylthiophene [1] gives m.p. 128-129°.

Heating of 2,5-di-(chloromercuri)-3-methylthiophene with 20% hydrochloric acid gave 4.4 g pure 3-methylthiophene: b.p. 115.1-115.4° (755 mm); n_D^{20} 1.5207; d_4^{20} 1.0203; MR_D 29.28. $C_5H_6S\ulcorner_2$. Calculated: MR_D 29.96.

Found %: S 32.59, 32.66. C_5H_6S. Calculated %: S 32.67.

A comparison of the constants of the two preparations of 3-methylthiophene (that obtained from the product of reaction by distillation in a column and that obtained from 2,5-di-(chloromercuri)-3-methylthiophene) indicates the high degree of purity of the first preparation.

3) 2-Ethylthiophene from n-Hexyl Alcohol

104 g (150 ml) catalyst; tube with inner diameter of 20 mm. The n-hexyl alcohol [b.p. 155-156° (757 mm); n_D^{20} 1.4210; d_4^{20} 0.8199] was introduced in a stream of sulfur dioxide at 450°. The first two experiments were run in identical conditions and their catalyzates were worked up together. The experimental conditions and the results of fractional distillations are set forth in Table 2.

The yield of 2-methylthiophene was calculated on the basis of the 4th fraction (reckoned on alcohol used) and that of 2-ethylthiophene on the basis of the 6th fraction; the 8th fraction was unchanged hexyl alcohol. The average yield of thiophene present in the first and second fractions was 2%; it was determined from the weight of the 2nd fraction and from the chloromercuri derivative of thiophene subsequently prepared from the first fraction.

The first fractions from all the four experiments were combined and distilled in a column with an efficiency of 40 theoretical plates, the following being isolated:

a) 12.9 g of a mixture of hexenes with b.p. 62.5-69.0° (742 mm).

Found %: C 85.60, 85.49; H 14.55, 15.51. C_6H_{12}. Calculated %: C 85.63; H 14.37.

b) 10.4 g with b.p. 78.5-81.0° (742 mm), mercuration of which gave 9.1 g 2,5-di-(chloromercuri)-thiophene and 12.2 g 2-chloromercurithiophene with m.p. 183-184° (no depression in mixed melting test with pure 2-chloromercurithiophene). Decomposition of the chloromercuri derivatives of thiophene with 20% hydrochloric acid gave 3.5 g pure thiophene b.p. 83.5-84° (754 mm); n_D^{20} 1.5246; d_4^{20} 1.0615; MR_D 24.27. $C_4H_4S\ulcorner_2$. Calculated: MR_D 25.34.

TABLE 2 (CONT.)

(in g) of fractions of catalyzate						Yields (%)		
4	5	6	7	8	residue	2-methylthiophene	2-ethylthiophene	n-hexyl alcohol
111-118°	118-130°	130-140°	140-151°	151-155°		(4th fraction)	(6th fraction)	(8th fraction)
6.4	0.6	5.9	0.3	29.3	1.5	4	3.3	15.2
3.6	0.7	1.3	0.3	17.9	1.5	4.5	1.4	17.5
2.4	0.3	0.6	0.3	15.9	1.6	2.9	0.6	15.6

Fractions 2 to 7 from all the experiments were fractionated in a column with an efficiency of 25 theoretical plates to give the 8 fractions listed in the table below.

	B.p. 769 mm	n_D^{20}	d_4^{20}	Wt. (in g)
1	67-84°	1.4880	0.9813	2.1
2	84.0-112.5	1.5019	1.0012	1.9
3	112.5-113.4	1.5185	1.0139	7.6
4	113.4-115.5	1.5198	1.0142	3.2
5	115.5-134.1	1.5068	0.9805	1.8
6	134.1-134.5	1.5022	0.9696	0.9
7	134.5-136.5	1.5007	0.9682	3.5
8	136.5	1.5026	0.9684	1.4
	Residue	—	—	1.0

The first fraction contained thiophene; the third and fourth were 2-methylthiophene; the sixth, seventh, and eighth were 2-ethylthiophene.

Mercuration of 1.4 g of the first fraction gave 0.7 g 2-chloromercurithiophene with m.p. 183-184° (no depression observed in mixed test with authentic 2-chloromercurithiophene) and 2.4 g 2,5-di-(chloromercuri)-thiophene.

Found %: Hg 72.48, 72.59. $C_4H_2SHg_2Cl_2$. Calculated %: Hg 72.38.

From 8.4 g mixture of third and fourth fractions was obtained 23 g 5-chloromercuri-2-methylthiophene with m.p. 204.0-204.5°.

Found %: Hg 60.47, 60.39. C_5H_5SHgCl. Calculated %: Hg 60.20.

Heating of 21.5 g 5-chloromercuri-2-methylthiophene with 20% hydrochloric acid gave 5 g 2-methylthiophene with b.p. 112.3-112.5 (754 mm); n_D^{20} 1.5210; d_4^{20} 1.0202; MR_D 29.30. $C_5H_6S\digamma_2$. Calculated: MR_D 29.96.

Found %: S 32.50, 32.57. C_5H_6S. Calculated %: S 32.67.

Literature data for 2-methylthiophene [10]: b.p. 112.5° (760 mm); n_D^{20} 1.5203; d_4^{20} 1.0194; m.p. of 5-chloromercuri-2-methylthiophene [1] 204-205°.

3.8 g of mixture of seventh and eighth fractions gave 8.0 g 5-chloromercuri-2-ethylthiophene with m.p. 147-148°

Found %: Hg 57.76, 57.67. C_6H_7SHgCl. Calculated %: Hg 57.77.

Heating of 6.7 g 5-chloromercuri-2-ethylthiophene with 20% hydrochloric acid gave 0.92 g 2-ethylthiophene: b.p. 135.5-136.5° (758 mm); n_D^{20} 1.5137; d_4^{20} 0.9928; MR_D 34.00. $C_6H_8S\digamma_2$. Calculated: MR_D 34.57.

Found %: S 28.41, 28.50. C_6H_8S. Calculated %: S 28.58.

Literature data for 2-ethylthiophene [11]: b.p. 133.0-134.5°; n_D^{20} 1.5122; [12]: d_4^{20} 0.922; m.p. of 5-chloromercuri-2-ethylthiophene [1]: 146-147°.

SUMMARY

1. Interaction of n-butyl, isoamyl or n-hexyl alcohols with sulfur dioxide in presence of chromia-on-alumina leads to thiophene and its homologs respectively.

2. In optimum conditions the yield of thiophene from n-butyl alcohol reached 10%; the yield of 3-methylthiophene from isoamyl alcohol reached 12.4%; the yields of 2-ethylthiophene, 2-methylthiophene and thiophene

from n-hexyl alcohol were, respectively, 3.3, 4 and 2%.

3. In the preparation of thiophene by the action of sulfur dioxide on a wet mixture of the butenes formed by dehydration of n-butyl alcohol, the yield of thiophene was 33% (reckoned on the alcohol).

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UNSATURATED CYCLIC HYDROCARBONS AND THEIR HALOGEN DERIVATIVES

XIII. THE MECHANISM OF CONJUGATED HALOGENATION AND DEHALOGENATION

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In our previous communications [1, 2] it was shown that the transformation of 1,2-dibromocyclohexane into benzene by heating with quinoline actually takes place through the intermediate formation of 1,3-cyclohexadiene and of perbromides of quinoline (products of addition of bromine and hydrogen bromide to quinoline). These observations confirmed the first and second stages of the scheme that one of us [3] had proposed for transformation of polyhalo derivatives of cyclohexane into aromatic compounds when heated with quinoline.

We could have confirmed the third stage of the scheme if we had isolated 1,4-dibromocyclohexene-2 in the reaction of 1,2-dibromocyclohexane with quinoline. We failed to achieve this, however, both in this reaction and in the reaction of 1,3-cyclohexadiene with hexabromoethane and quinoline [1]. For the purpose of demonstrating the third stage of the proposed scheme, we carried out the reaction of 1,3-cyclohexadiene, in the absence of free quinoline, with a series of quinoline perbromides: quinoline hydrobromide dibromide, quinoline tetrabromide and quinoline dibromide; these compounds, in our opinion, could be formed in the conditions of conjugated halogenation and dehalogenation.

It was established that heating of 1,3-cyclohexadiene with quinoline hydrobromide dibromide gives exclusively tetrabromocyclohexane, while in the cold a mixture of dibromocyclohexene and tetrabromocyclohexane is obtained. In the cold with quinoline tetrabromide, a crystalline product is obtained which consists of a mixture of approximately equal parts of dibromocyclohexene and tetrabromocyclohexane. In the cold with quinoline dibromide, the product is dibromocyclohexene free from tetrabromocyclohexane.

The tetrabromocyclohexane is evidently 1,2,3,4-tetrabromocyclohexane. The dibromide is very probably 1,4-dibromocyclohexene-2 since systems containing conjugated double bonds possess a great tendency to undergo addition reactions in the 1,4-position. Moreover, the investigation of Farmer and Scott [5] have shown that 1,2-dibromocyclohexene-3 may be obtained by addition of bromine to 1,3-cyclohexadiene at −15° and only with maintenance of a number of other conditions. The authors showed that it isomerizes very easily into 1,4-dibromocyclohexene-2 when heated and that this process even takes place spontaneously on keeping.

All our attempts to confirm the structure of the dibromocyclohexene prepared with quinoline dibromide have so far been unsuccessful. Ozonization of the bromide gave a very unstable ozonide. After complete removal of the solvent (chloroform) it spontaneously ignited. When the solvent is not completely eliminated, the ozonide is decomposed by water with great difficulty, and titration with alkali leads to formation of very glutinous, ropy films which appeared to consist of a polymeric product although it defied further examination. Oxidation with potassium permanganate solution at room temperature also failed to throw light on the structure of this dibromide. Oxidation was performed in presence of the calculated amount of potassium bisulfate in order to avoid the extremely undesirable alkaline reaction of the medium, since two bromine atoms (in 1,4-dibromocyclohexene-2) or one (in 1,2-dibromocyclohexene-3) in the dibromocyclohexene formed are allylic. Oxidation was accompanied by evolution of bromine which was clearly detected by the odor. Oxidation gave (apart from unchanged dibromocyclohexene) only succinic acid, which could have been formed either by oxidation of 1,4-dibromocyclohexene-2 or of 1,2-dibromocyclohexene-3.

Attention must be drawn to the fact that the attempts of a number of investigators to establish the structure of the dibromocyclohexene with m.p. 108°, and believed to be 1,4-dibromocyclohexene-2, have likewise not met with success [4, 5, 6, 18]. The work of Ziegler [18], however, makes it probable that in this dibromide the bromine atoms are in the 1,4-position and not in the 1,2-position.

In our latest investigation we studied the action of quinoline on the crystalline dibromides obtained by reaction of 1,3-cyclohexadiene with each of the quinoline perbromides in order to establish whether they are capable of transformation into aromatic compounds under the action of quinoline, i.e., in order to establish whether the bromides formed are indeed intermediate products during conjugated halogenation and dehalogenation, as should follow from the fourth stage of the scheme. With this objective, each of the above-noted crystalline products was heated with quinoline. The following facts emerged from a study of the ultraviolet absorption spectra: a) Quinoline reacts with the tetrabromocyclohexane obtained by heating 1,3-cyclohexadiene with quinoline hydrobromide dibromide to give a product containing about 90% bromobenzene; the action of quinoline on the crystalline product consisting mainly of dibromocyclohexene (obtained by reaction in the cold) gives nearly pure benzene; b) the product of interaction of 1,3-cyclohexadiene with quinoline tetrabromide reacts with quinoline in the cold to form a mixture of benzene and bromobenzene; c) treatment with quinoline of the crystals isolated on interaction of 1,3-cyclohexadiene with quinoline dibromide leads to a product containing about 90% benzene.

The formation of dibromocyclohexene by interaction of 1,3-cyclohexadiene with quinoline perbromides and the formation therefrom, by the action of quinoline, of benzene is evidence that dibromocyclohexene may indeed be an intermediate product in conjugated halogenation and dehalogenation. This is in accord with the third and fourth stages of the scheme which was advanced by one of us but which could not previously be confirmed.

EXPERIMENTAL

Reaction of 1,3-Cyclohexadiene with Quinoline Perbromides

Experiments were performed with cooling with iced water in a flask fitted with dropping funnel and reflux condenser. It should be noted that in the preparation of the dibromocyclohexene in which we are interested, it is more advantageous not to add the 1,3-cyclohexadiene dropwise to the quinoline perbromide (although this is more convenient) but to adopt the opposite procedure, even though experimentally less convenient: To the 1,3-cyclohexadiene (the amount varied from 3.5 to 8 g in different experiments) is added the quinoline perbromide in small portions through the reflux condenser. The smaller these portions the less is the product resinified and the smaller its content of tetrabromocyclohexane. With the reverse order of addition of the reactants, a mixture is formed of dibromocyclohexene and a fairly considerable amount of tetrabromocyclohexane. In all probability, this is because when 1,3-cyclohexadiene is added dropwise to quinoline perbromide, each drop of hydrocarbon comes into contact with a large quantity of quinoline perbromide which has a great tendency to release bromine atoms (exothermal reaction). This gives rise to local over-heating which can facilitate both addition of four atoms of bromine to the 1,3-cyclohexadiene and excessive resinification.

1,3-Cyclohexadiene was prepared by a slight modification of the method of Hofmann and Damm [7]: instead of sodium ethylate we used a saturated solution of alcoholic alkali.

The quinoline required for preparation of quinoline perbromides was obtained by Skraup's synthesis.

1. Reaction of 1,3-cyclohexadiene with quinoline hydrobromide dibromide. Reaction with heating. Quinoline hydrobromide dibromide was prepared by a slight modification of the methods of Rosenmund [8] and Trowbridge [9]. 5 g quinoline was cooled in a round-bottomed flask; careful addition was made of 3.2 ml concentrated hydrochloric acid, the contents of the flask then crystallizing in the form of a snowy-white mass; gradual addition was then made of 42 ml iced water; the solution of quinoline hydrochloride was thoroughly cooled and 2.9 ml bromine was introduced. The pomegranate-red crystals of perbromide were filtered off, pressed and used for reactions without recrystallization.

6.2 g 1,3-cyclohexadiene was added in small portions to an equimolar amount of quinoline perbromide. The mixture was heated for 1-2 hours on an oil bath at 120-145°; the contents of the flask formed two opaque layers. The upper layer gave a very weak emulsion with water and an extremely minute amount of oil separated when treated with alkali solution. The lower layer was a brown-colored oily liquid much contaminated with resin; it was much heavier than water and not appreciably soluble in water. When washed with water (the wash liquor had an acidic reaction) it partly crystallized in the form of very hard crystals which after two recrystallizations from alcohol melted at 70-71.5°; weight 7.5 g (preparation I). Found: M 385.3, 378.6; % Br 80.23, 80.53. $C_6H_8Br_4$. Calculated: M 399.88; % Br 79.99.

For 1,2,3,4-tetrabromocyclohexane the literature data are: m.p. 87-89° [10], 87-88° [7, 12], 140-141° [10, 11], 90-92° [13], 155-156° [10], 184° [13, 14].

We see that the melting point of our crystals is lower than the lowest melting point reported in the literature for the tetrabromides prepared from 1,3-cyclohexadiene. We evidently obtained one of the six possible stereoisomers of 1,2,3,4-tetrabromocyclohexane.

5 g 1,3-cyclohexadiene was added to an equimolar quantity of quinoline perbromide. The mixture was heated on an oil bath for 50 minutes at 100-110°. The lower layer was collected. Weight 11.1 g, brownish-black in color, did not form an emulsion with water; the wash liquor did not have an acid reaction. The unreacted hydrocarbon was drained off in vacuum, after which 4 g crystals separated from the oil. After three recrystallizations from alcohol they formed pinkish-yellow leaflets with m.p. 84.3-86.9°.

Found %: M 392.8, 404.8; % Br 80.25, 80.38. $C_6H_8Br_4$. Calculated: M 399.88; % Br 79.99.

Reaction in the cold. To 6.9 g 1,3-cyclohexadiene, cooled with iced water, was added through the reflux condenser 31 g quinoline perbromide in small portions. With progressive addition of the perbromide two layers formed in the flask; the nearly colorless upper layer had a quinoline odor, formed a weak emulsion with water, and did not give an acidic reaction; the lower layer (brown-red) did not give an emulsion with water and immediately settled to the bottom. Weight 20.3 g instead of 20.7 g calculated for the dibromocyclohexene formed. After standing for a short period the oil crystallized. The crystals were washed with alcohol. Recrystallization was not carried out to avoid loss of any components of the reaction mixture. Colorless, lachrymatory crystals (13.2 g) with m.p. 58-84° (preparation II).

Found: M 255.0, 265.5; % Br 69.45, 69.13. $C_6H_8Br_2$. Calculated: M 239.95; % Br 66.60.

The high bromine content found may be explained by the formation of higher bromo derivatives at the same time.

2. Interaction of 1,3-cyclohexadiene with quinoline tetrabromide in the cold. Quinoline tetrabromide was obtained in the form of a friable crystalline mass by Grimaux's method [15]: addition of 12 ml bromine, with cooling, to an emulsion of 15.2 g quinoline in 45 ml water; the product was utilized without recrystallization.

To 2.3 g 1,3-cyclohexadiene was added 13 g quinoline perbromide. Two layers formed in the flask. The upper one was nearly colorless, did not give an emulsion with water and had a neutral reaction; alkali solution brought down quinoline. The lower layer (8.9 g instead of the required 6.9 g of dibromocyclohexene) crystallized. After recrystallization from alcohol, the weakly lachrymatory, pinkish-yellow crystals melted at 60-88° (preparation III).

Found: M 315.3, 322.2; % Br 73.55, 73.90. $C_6H_8Br_2$. Calculated: M 239.95; % Br 66.60. $C_6H_8Br_4$. Calculated: M 399.88; % Br 79.99.

3. Interaction of 1,3-cyclohexadiene with quinoline dibromide in the cold. To a well-cooled emulsion of 12.5 g quinoline in 40 ml water was added, from a dropping funnel with very energetic stirring, 5.1 ml bromine. The orange-red crystalline mass was filtered off and pressed between sheets of filter paper (34 g instead of 28.5 g). The perbromide had m.p. 60-67°. Compare [19, 20, 21].

0.1696 g substance: 0.1992 g AgBr. 0.2049 g substance: 0.2412 g AgBr. Found %: Br 49.98, 50.10. $C_9H_7NBr_2$. Calculated %: Br 55.34.

The low percentage of bromine and the higher weight of perbromide than is required by the formula $C_9H_7NBr_2$ may be due to the same cause, namely addition of water to the quinoline dibromide molecule. Repeated observations led us to this conclusion. Thus, instead of 7 g quinoline dibromide we obtained 8.6 g; instead of 14 g we obtained 17.3 g, and so forth. Calculated: content of Br for $C_9H_7NBr_2 \cdot H_2O$ 52%; for $C_9H_7NBr_2 \cdot 2H_2O$ 49.2%.

After the reaction of quinoline dibromide with the unsaturated hydrocarbon, the water of hydration separates and collects in the form of a layer above the bromide formed from the hydrocarbon in the quinoline. The weight approximately corresponds to the observed excess over the theoretically calculated value for the preparation of quinoline dibromide.

To 7 g 1,3-cyclohexadiene was added with cooling, 25 g quinoline dibromide. The upper (colorless) layer weighed 12.2 g, did not give an emulsion with water and separated an insignificant amount of quinoline when treated with alkali. The lower layer (brown) weighed 20 g and crystallized. The crystals (repeatedly washed with alcohol) weighed 9.4 g; pink color, lachrymatory; m.p. 85-95° (preparation IV).

0.4530 g substance: 16.64 g benzene: Δt 0.574°. 0.3621 g substance; 16.64 g benzene: Δt 0.462°. 0.1920 g substance: 0.2993 g AgBr. 0.2003 g substance: 0.3130 g AgBr. Found: M 243.3, 241.6; % Br 66.34, 66.50. $C_6H_8Br_2$. Calculated: M 239.95; % Br 66.60.

The wide melting range of the crystals may be due to the formation in the given conditions of both of the possible 1,4-dibromocyclohexenes-2. We regard the formation of 1,2-dibromocyclohexene-3 in our reaction conditions to be very improbable in the light of the results of Farmer and Scott.

Action of Quinoline on the Bromides Obtained from 1,3-Cyclohexadiene and Quinoline Perbromides

4. Action of quinoline on the tetrabromide (I). 12 g tetrabromocyclohexane was very slowly and carefully heated in a Wurtz flask with 17 g quinoline until the first signs of start of reaction were observed; the heating was temporarily stopped at that point until the vigorous reaction had ceased. The distilled oil (3.4 g) was washed with dilute sulfuric acid and then with water and dried with calcium chloride before distillation. The fraction with b.p. 153-155° had d_4^{18} 1.5041 and n_D^{18} 1.5607.

The ultraviolet absorption spectrum showed that the product contained 90-95% bromobenzene.

5. Action of quinoline on bromide (II). 17.7 g crystals and 28 g quinoline were carefully heated until the first signs of reaction which afterwards proceeds very vigorously with evolution of much heat. The distillate (6.1 g) was washed with dilute sulfuric acid and water, dried with calcium chloride and metallic sodium and distilled.

The fraction with b.p. 79-82° (2.5 g) was a transparent liquid which crystallized below −8°; its constants were in fairly good agreement with those of benzene and the ultraviolet absorption spectrum indicated that it was about 90% benzene.

Bromine number by the McIlinnhey method [17] 1.0; $d_4^{17.3}$ 0.8848; $n_D^{17.3}$ 1.5023.

6. Action of quinoline on (III). To 8.1 g of the crystals obtained according to section 2 above was added 10 g quinoline. The mixture was cautiously heated until the reaction started. The distilled product was washed with dilute sulfuric acid and water and dried with calcium chloride. It boiled over the wide temperature range of 76-150° (1.95 g). The spectroscopic examination revealed a different absorption than for the 1,3-cyclohexadiene taken for reaction with quinoline tetrabromide; the absorption band has the fine structure characteristic of benzene but is blurred by its overlapping with the absorption of bromobenzene.

7. Action of quinoline on (IV). 8 g of the bromide prepared in section 3 above and 12 g quinoline were cautiously heated in a Wurtz flask until the reaction started; it then proceeded intensively without heating. The distillate, coming over at 78-120°, was washed with dilute sulfuric acid and water and dried with calcium chloride. After two distillations over metallic sodium (to bind the bromides) a transparent liquid was obtained which crystallized at −5 to −7° and did not contain halogen. Weight 1.8 g or 69.1%.

B.p. 78-82°; bromine number 4.0; d_4^{16} 0.8800; n_D^{16} 1.5017. The spectroscopic examination indicated a content of 90-95% benzene.

SUMMARY

1. Interaction of 1,3-cyclohexadiene with quinoline dibromide gives dibromocyclohexene. It is shown that quinoline acts on the bromide formed to give benzene.

2. Heating of quinoline hydrobromide dibromide with 1,3-cyclohexadiene gives tetrabromocyclohexane. Among the products of interaction of the tetrabromide with quinoline is bromobenzene.

3. The main product of reaction of 1,3-cyclohexadiene with quinoline hydrobromide dibromide in the cold is dibromocyclohexene.

4. Reaction of 1,3-cyclohexadiene with quinoline tetrabromide in the cold leads to a mixture of approximately equal parts of dibromocyclohexene and tetrabromocyclohexane.

5. The experimental data are in full accord with the scheme previously put forward by one of us [3] and may serve as confirmation of the last two stages of the scheme.

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THE ACTION OF AMMONIA ON 1-HYDROXYANTHRAQUINONE

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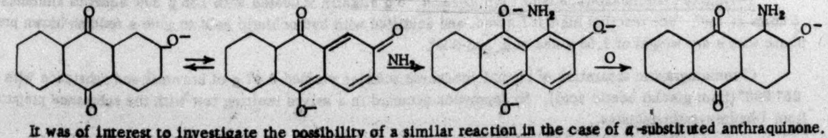
Derivatives of anthraquinone containing amino groups in the α-position, especially 1-amino- and 1,5-diaminoanthraquinones, are most important starting materials for the synthesis of other dyes (vat and acid dyes for acetate and synthetic fiber and pigment dyes). The only technical method for the preparation of these derivatives is the ammonolysis of the corresponding anthraquinone sulfonic acids. However, not even the most successful industrial methods of preparation secures complete transformation of the sulfonic acid into amino compound [1]. A yield of 100% 1-aminoanthraquinone represents 62% of the theoretical; a yield of 100% 1,5-diaminoanthraquinone represents 62% of the theoretical.

Due to the high concentration of hydroxyl ions in aqueous ammonia, formation of hydroxy derivatives of anthraquinone is always observed, as well as substitution of the sulfo group by the amino group.

Attention to the absence of a fully satisfactory method of preparation of 1-aminoanthraquinone was drawn by Fierz-David [2] in his well-known book.

A patent was recently announced for the preparation of α-amino derivatives of anthraquinone by heating the corresponding sulfonates with ammonium salts of arsenic acid at pH values in the vicinity of 7, which enables the preparation of amino derivatives of high quality; the yield of 1-aminoanthraquinone reaches 98.7% (at pH 7.3) and that of 1,5-diaminoanthraquinone 85% (at pH 7) [3]. This method is inconvenient, however, on the industrial scale, because of the employment of a large amount of arsenic compounds.

In a study of the ammonolysis of 2-chloroanthraquinone by aqueous ammonia [4], one of us found that the principal by-product of the reaction, which is soluble in aqueous ammonia, is 1-amino-2-hydroxyanthraquinone. It transpired that on interaction of 2-hydroxyanthraquinone with ammonia in milder conditions than those necessary for transformation of 2-chloroanthraquinone into 2-aminoanthraquinone, substitution of hydrogen takes place in the 1-position of the anthraquinone nucleus. Simultaneously, the carbonyl groups are reduced as in the well-known addition of ammonia and amines to benzoquinone.



It was of interest to investigate the possibility of a similar reaction in the case of α-substituted anthraquinone.

Heating of 1-hydroxyanthraquinone with ammonia gave a product soluble in alkalies and containing nitrogen. Chromatographic separation of the chlorobenzene solution of this product on alumina as the sole component yielded a substance with m.p. 257-258° and with an elementary analysis corresponding to an aminohydroxyanthraquinone.

Regarding here, as in the case of 2-hydroxyanthraquinone, the process of substitution of hydrogen by the amino group as the addition of ammonia to the tautomeric form of the hydroxyanthraquinone ion, we can expect the amino group to enter the anthraquinone nucleus in the 2-, 3-, or 4-position. We know that in the action of aniline on o-benzoquinone, the phenylamino group enters in the para-position to the carbonyl groups [5]. In the action of metal arylides on α-amino derivatives of anthraquinone, substitution of hydrogen occurs in the 4-position [6]. Alkaline fusion of 1-hydroxyanthraquinone, which must be regarded as an analogous process, leads to formation of alizarin [7].

The substance obtained by the action of aqueous ammonia on 1-hydroxyanthraquinone had properties similar to those of 1-hydroxy-2-aminoanthraquinone. The latter was synthesized by Perger, Scholl and others by reacting aqueous ammonia with alizarin [8]; Benda prepared it from 3-nitro-4-hydroxy -1-anthraquinonyl-arsonic acid (m.p. about 250°) [9]: Kopetschni prepared it from 2-acetamino-1-acetoxyanthraquinone (m.p. 257-258°) [10]: Brass and Ziegler prepared it by decomposition of 2-anthraquinonyl-alizarin in concentrated sulfuric acid (m.p. 226-227°) [11].

With the aim of identifying the prepared compound, the synthesis was effected of 1-hydroxy-2-aminoanthraquinone by amination of alizarin followed by purification of the product by chromatography on alumina. The purified substance melted at 257-258° and proved to be identical with the compound prepared from 1-hydroxyanthraquinone.

Consequently, the main direction of the reaction of 1-hydroxyanthraquinone with aqueous ammonia may be represented by a scheme of the above type.

1-Hydroxy-2-aminoanthraquinone was detected among the products of ammonolysis of 1-anthraquinonesulfonic acid. The products soluble in aqueous ammonia were isolated by acidification and were chromatographed on alumina in chlorobenzene solution. Chromatographic examination of technical 1-aminoanthraquinone likewise revealed the presence of 1-hydroxy-2-aminoanthraquinone.

EXPERIMENTAL

1-Hydroxyanthraquinone was prepared by diazotization of 1-aminoanthraquinone and decomposition of the diazo compound by Ullmann's method [12]; m.p. 191-192°.

1-Hydroxy-2-aminoanthraquinone from 1-hydroxyanthraquinone. 20 g 1-hydroxyanthraquinone is heated for 6 hours at 131-140° with 273 g 25% aqueous ammonia. To the reaction mass is added 50 ml 2% sodium hydroxide solution, thoroughly stirred and filtered. An insoluble black precipitate is collected on the filter. The violet solution is acidified with hydrochloric acid and a reddish-brown flocculent precipitate is formed. Weight of dry precipitate 1.35 g, m.p. 218-223°. Treatment of the insoluble precipitate with 1500 ml 2% sodium hydroxide at 60° followed by acidification of the solution gives an additional 0.35 g reddish-brown product with m.p. 207-224°. The precipitates are combined. A solution of 1.2 g of the mixture in 1900 ml chlorobenzene is subjected to chromatographic separation on alumina. Several colored bands are formed. The main broad band (blue-violet) is separated and the adsorbed substance is eluted with 4% sodium hydroxide solution. Acidification of the reddish-violet alkaline solution gives 0.5 g brown-red material with m.p. 257-258° (from glacial acetic acid). The compound dissolves in alcohol with a yellowish-red color, in ether with an orange color, in NaOH solution with red-violet color and in concentrated sulfuric acid with a brown color (according to Brass and Ziegler the solution in concentrated sulfuric acid is olive green). It readily forms a hydrosulfite-alkali vat with an orange color. With baryta water it gives an insoluble blue-violet precipitate.

Found %: C 69.51, 70.71; H 3.92, 3.94; N 6.18, 6.25. $C_{14}H_9O_3N$. Calculated %: C 70.27; H 3.79; N 5.86

1-Hydroxy-2-aminoanthraquinone from alizarin. 8 g alizarin is heated with 135 g 30% aqueous ammonia for 5 hours at 150°. The reaction mass is filtered, and acidified with hydrochloric acid to give a reddish-brown precipitate with a dry weight of 1.55 g and m.p. 218-234°.

Chromatographic separation of the chlorobenzene solution yielded 0.47 g of brownish-red substance with m.p. 257-258° (from glacial acetic acid). No depression occurred in a mixed melting test with the substance prepared from 1-hydroxyanthraquinone.

Found %: C 69.94, 69.73; H 4.02, 3.93; N 5.91, 6.05. $C_{14}H_9O_3N$. Calculated %: C 70.27; H 3.79; N 5.86.

SUMMARY

1. The action of aqueous ammonia on 1-hydroxyanthraquinone gives 1-hydroxy-2-aminoanthraquinone.

2. 1-Hydroxy-2-aminoanthraquinone is formed as a by-product in the ammonolysis of 1-anthraquinonesulfonic acid.

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ACYLATION WITH THE AID OF VINYL ACETATE

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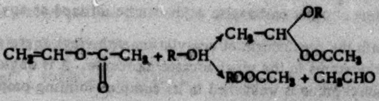
We have previously described the interaction of vinyl acetate with amines [1] which showed vinyl acetate to be a convenient acetylating agent with selective action.

M. F. Shostakovsky showed [2] that in presence of mercuric salts alcohols add on to vinyl acetate at the double carbon-carbon bond with formation of acetates of polyacetals (so-called acylals), whereas in the case of tertiary alcohols, acetates are obtained.

Consequently, depending upon the structure of the original alcohol, the reaction may proceed in two directions



$$CH_2{=}CH{-}O{-}\underset{\underset{O}{\|}}{C}{-}CH_3 + R{-}OH \begin{cases} \nearrow CH_3{-}CH\begin{matrix} OR \\ OOCCH_3 \end{matrix} \\ \searrow ROOCCH_3 + CH_3CHO \end{cases}$$

It is reported in the patent literature that secondary alcohols [3] and phenols, in presence of alkaline agents, are acetylated by vinyl acetate.

We carried out several experiments on the interaction of vinyl acetate with alcoholates and found that by this means it was possible to acetylate not only secondary but also primary alcohols. The reaction proceeds very energetically and is accompanied by polymerization, as well as by secondary formation of sodium acetate (even when the reaction is performed with cooling or in solvents), so that excess of vinyl acetate is needed for satisfactory yields.

Regarding the character of the polymer formed, it is evidently an alcoholate of polyvinyl alcohol since it dissolves easily in water and alcohol.

It proved to be most advantageous to use as the solvent an excess of the alcohol to be acetylated, which itself does not react with vinyl acetate. All the experiments were run in comparable conditions, i.e., to the prepared alcoholate (0.05 g-atom sodium was dissolved in 0.1 mole alcohol) was carefully added 0.1 mole vinyl acetate at 0°.

It was found that furfuryl alcohol, which possesses an allenic structure, gives a nearly quantitative yield of acetate (reckoned on the alcoholate brought into reaction), but in the same conditions allyl alcohol gives only a considerable amount of resin, possibly due to copolymerization both of the alcohol itself and of its acetate with the vinyl compounds. Still more interesting is the fact that cyclohexanol gave a good yield of acetate – 40.5% of the theoretical (81% reckoned on the alcoholate) – whereas 3-hexanol, which contains the same number of carbon atoms and is also a secondary alcohol, is totally recovered from the reaction unchanged. In the case of β-phenylethyl alcohol, the acetate is obtained in a yield of 18% of the theoretical (36% reckoned on the alcoholate).

By analogy with isopropenyl acetate [5] we attempted to perform the acetylation of alcohols with the help of acidic agents. By heating in presence of sulfuric acid, vinyl acetate was also found to acetylate alcohols. In these conditions phenol gives a product of the polycondensation type (phenol-aldehyde resins). Acetylation of isopropyl alcohol (yield 39%) and of dimethylethylcarbinol (yield 43%) is accompanied by formation of a considerable amount of olefin (due to dehydration).

In all the experiments, the catalyst was used in the proportion of 3-5% by weight of the alcohol; the alcohol and vinyl acetate were in equivalent amounts. The mixture of components was heated 6-8 hours to 100-110°.

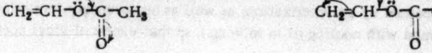
In these conditions allyl alcohol is appreciably resinified and enters incompletely into the reaction; the yield is 22% of the theoretical (40% reckoned on the alcohol used); cyclohexanol gives 35% (65%) yield; 1-ethoxy-2-propanol 35% (68%); 1-hexanol 49% (80%).

With 1-hexanol several experiments were carried out with the objective of establishing the effect of both the conditions and the catalysts on the yield of acetate. It was found that the introduction of double the amount of vinyl acetate raised the yield to 69%. Other catalysts were also tried out. In presence of aluminium sulfate the yield was 64% (for equivalent amounts of alcohol and vinyl acetate). Aluminum ethylate was also tried since we thought that the acetaldehyde would partially disproportionate by a Tishchenko reaction [6] and thereby appreciably raise the yield of acetate. Aluminum ethylate proved, however, to be too weak a catalyst. The yields did not exceed 12%. Ethyl acetate was not detected among the products of the reaction in experiments in an open vessel or in sealed ampoules.

Consequently, vinyl acetate can serve as a convenient acetylating agent for amines and alcohols. Due, however, to its selectivity, it has some advantages over ketenes, although the yields of acetates in our case are considerably lower. We, therefore, decided to test the acetylating action of vinyl esters of other acids in cases where the preparation of the corresponding ketene is either impossible or involves great difficulties. From vinyl acetate we therefore prepared vinyl butyrate and vinyl benzoate by treatment with the respective alcohols in presence of mercuric salts [5, 7]. It was found that vinyl butyrate, in analogy with vinyl acetate, readily forms butyraldehyde together with little resin (with equivalent amounts the yield is 70%). In the absence of catalyst, vinyl benzoate does not react with aniline at room temperature; the addition of a little sulfuric acid, however, provokes a vigorous reaction and the yield of benzanilide, with equimolar quantities, reaches 82%. Consequently, not only vinyl acetate, but also vinyl esters of other carboxylic acids can be utilized as acylating agents.

In order to explain the mechanism of acetylation with vinyl acetate, we must take into consideration the reciprocal influence of the atoms in the vinyl acetate molecule. It is obvious that the oxygen atom located between the vinyl and the carbonyl group is weakened in its complex-forming properties due to the influence of the carbonyl group, and nucleophilic agents will be the most likely to attack the carbonyl carbon atom. This is actually observed in the action of amines or alcoholates.

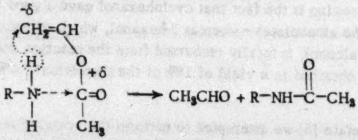
The matter is rather more complicated when we consider the vinyl portion of the molecule, which likewise influences the ethereal oxygen atom and even more reduces its ability to form oxonium salts.



$$CH_2{=}CH{-}\ddot{O}{-}\underset{\underset{O}{\|}}{\overset{+\delta}{C}}{-}CH_3 \qquad CH_2{=}CH{-}\ddot{O}{-}\underset{\underset{O}{\|}}{C}{-}CH_3$$

It follows from the above schemes that the CH_2 group in the vinyl acetate molecule is rather more electronegative than the CH group and, consequently, electrophilic agents are bound to preferentially attack the methylene group, although the carbonyl group also weakens the above-indicated polarization of the bond.

In practice, the action of strong acids on vinyl acetate (proton attack) leads to cleavage of acetaldehyde. The mercury group also acts on the methylene and not on the methine group [8]. Finally, sulfonation of vinyl butyl ether and of vinyl acetate by pyridine- and dioxanesulfotrioxide [9] leads to sulfoacetaldehyde, which fact also is consistent with the presence of a certain negative charge at the methylene group. Consequently, if nucleophilic agents (such as amines) attack vinyl acetate, then acetylation takes place. At first, the nucleophilic agent attacks the carbonyl carbon atom, while subsequently we get stabilization of the intermediate complex due to migration of a proton and cleavage of a molecule of acetaldehyde.



$$R{-}\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{N}}\!\dashrightarrow \underset{\underset{CH_3}{|}}{\overset{\overset{O-CH{=}\overset{-\delta}{C}H_2}{|}\,+\delta}{C}}{=}O \longrightarrow CH_3CHO + R{-}NH{-}\overset{\overset{O}{\|}}{C}{-}CH_3$$

The ease of acetylation is governed primarily not by the mobility of the hydrogen atom but by the nucleophilism of the agent.

In the interaction of vinyl acetate with alcohols, the direction of the process depends on the conditions and on the structure of the alcohol. The nucleophilic properties of alcohols are markedly weakened by the phenomenon of association (hydrogen bond). If this bond is broken (say by conversion of the alcohols into alcoholates), then acetylation will take place. This can be demonstrated by adding acidic agents which facilitate cleavage of acetaldehyde.

If, however, the reaction of vinyl acetate with alcohols proceeds in presence of mercury salts, the primary process is mercuration a the double carbon-carbon bond which leads ultimately not to acetates but to acylals. In the case, however, of tertiary alcohols, which are more strongly nucleophilic than primary alcohols, the principal process, even in presence of mercury salts, is acylation.

EXPERIMENTAL

Acetylation of isopropyl alcohol. Into a two-necked flask fitted with stirrer and reflux condenser was introduced 6.0 g (0.1 mole) isopropyl alcohol, 8.6 g (0.1 mole) vinyl acetate and 4 drops sulfuric acid. The mixture was heated for 8 hours with stirring on an oil bath at 100-110°. Propene, identified as dibromide, was detected in the escaping gases. After this period, the mixture was dried with potassium carbonate and distilled in a low column to give 4.0 g isopropyl acetate or 39% of the theoretical. B.p. 87.5-88° at 753 mm.

n_D^{20} 1.3715; d_4^{20} 0.8740; MR_D 26.77; calculated 26.94.

Acetylation of dimethylethylcarbinol. By the same procedure, starting from 8.8 g (0.1 mole) dimethylethylcarbinol and 8.6 g vinyl acetate in presence of sulfuric acid, 5.5 g acetate was obtained. Yield 42% of theoretical. B.p. 121-124° at 740 mm. A second distillation gave b.p. 124-125° at 749 mm.

n_D^{20} 1.4010; d_4^{20} 0.8740; MR_D 36.16; calculated 36.18.

Acetylation of allyl alcohol. From 11.6 g (0.2 mole) allyl alcohol and 17.2 g (0.2 mole) vinyl acetate in presence of 5-6 drops sulfuric acid was obtained 4.4 g allyl acetate (22% of the theoretical yield). B.p. 102-103° at 762 mm.

n_D^{20} 1.4043; d_4^{20} 0.9272; MR_D 26.41; calculated 26.47.

Literature data: b.p. 103-104°; n_D^{20} 1.40488; d_4^{20} 0.9276 [10].

On adding vinyl acetate (16.2 g) to sodium allylate (2.3 g sodium in 11.6 g allyl alcohol) at 0°, very serious resinificiation is observed and no allyl acetate could be isolated from the products of reaction.

Acetylation of 1-hexanol. A) The reaction was conducted as in the preceding experiments (in presence of sulfuric acid). From 10.3 g (0.1 mole) 1-hexanol and 8.6 g vinyl acetate (0.1 mole) was obtained, after fractionation, 4.1 g of the original alcohol and 7.0 g acetate. Yield 49% of the theoretical (80% reckoned on the alcohol consumed). On introducing into the reaction an excess of vinyl acetate (17.2 g) the yield rises to 69%. B.p. 169-170° at 767 mm.

n_D^{20} 1.4115; d_4^{20} 0.8770; MR_D 40.83; calculated 40.88.

Literature data: b.p. 169.2°; d_0^0 0.8902 [11].

B) A mixture of 10.3 g 1-hexanol and 8.6 g vinyl acetate was heated with 0.3 g anhydrous aluminium sulfate in a sealed ampoule for 20 hours at 100-105°. Fractional distillation gave 3 g acetaldehyde (b.p. 21-24°, silver mirror test) and 9.2 g acetate. Yield 64% of the theoretical. B.p. 167-168° at 749 mm; n_D^{20} 1.4110.

C) A mixture of 10.3 g 1-hexanol, 8.6 g vinyl acetate and 0.5 g aluminum ethylate was heated in a sealed ampoule for 20 hours at 100-105°. Fractional distillation gave 1.7 g acetate. Yield 12% of theoretical. B.p. 168-169° at 758 mm.

Acetylation of 3-hexanol. From 9.0 g (0.09 mole) 3-hexanol and 7.7 g (0.09 mole) vinyl acetate in presence of 5-6 drops sulfuric acid after 8 hours' heating on an oil bath was obtained 3.6 g original alcohol and 6.5 g acetate. Yield 47% of the theoretical (85% reckoned on the alcohol consumed). B.p. 149-150° at 758 mm.

n_D^{20} 1.4061; d_4^{20} 0.8670; MR_D 40.83; calculated 40.80.

Literature data: b.p. 149-151°; n_D^{20} 1.4037; d_4^{20} 0.8672 [12].

On adding vinyl acetate to a solution of the sodium compound of 3-hexanol, considerable heat was developed; after extraction, however, of the reaction mixture with absolute ether followed by distillation of the extract, the original 3-hexanol was recovered and none of its acetate was detected.

Acetylation of cyclohexanol. A) 20.0 g (0.2 mole) cyclohexanol is placed in a three-necked flask fitted with stirrer and reflux condenser; addition is made with stirring of 2.3 g (0.1 g-atom) sodium in small pieces. After the metal has dissolved (1 hour at 110°) dropwise addition is made with cooling to the mixture (cooled to 0°) of 17.2 g (0.2 mole) vinyl acetate. After dilution with ether and separation of the precipitate, the liquid is distilled to give 11.5 g acetate. Yield 40.5% of the theoretical (81% reckoned on the alcoholate). B.p. 96-97° at 85 mm.

n_D^{20} 1.4432; d_4^{20} 0.9664; MR_D 38.92; calculated 38.59.

B) A mixture of 10.0 g (0.1 mole) cyclohexanol, 8.6 g vinyl acetate (0.1 mole) and 5-8 drops concentrated sulfuric acid was heated with stirring on an oil bath at 100-110° for 8 hours. Distillation gave 5.0 g cyclohexyl acetate. Yield 35% of theoretical (65% reckoned on the alcohol consumed). B.p. 98-100° at 82 mm; n_D^{20} 1.4435; d_4^{20} 0.9665.

Acetylation of 1-ethoxy-2-propanol. From 10.4 g (0.01 mole) 1-ethoxy-2-propanol and 8.6 g (0.1 mole) vinyl acetate in presence of 5 drops sulfuric acid was obtained 5.1 g of the original alcohol and 3.2 g acetate. Yield 35% of theoretical (68% reckoned on the alcohol consumed). B.p. 164-165° at 758 mm.

n_D^{20} 1.4081; d_4^{20} 0.09456; MR_D 38.42; calculated 38.82.

Literature data: b.p. 158-160°; n_D^{20} 1.4097; d_4^{20} 0.9462 [13].

Acetylation of β-phenylethyl alcohol. In 12.2 g (0.1 mole) β-phenylethyl alcohol was dissolved 1.1 g (0.05 mole) metallic sodium. To the cooled (to 0°) mixture, dropwise addition was then made, with stirring and cooling of 8.6 g (0.1 mole) vinyl acetate. Sodium acetate was precipitated by adding ether and filtered off. Distillation of the filtrate gave 3.0 g acetate. Yield 18% of the theoretical (30% reckoned on the alcoholate). B.p. 110-111° at 18 mm.

n_D^{20} 1.5115; d_4^{20} 1.044; MR_D 47.14; calculated 46.43.

Literature data: b.p. 224°; 118-129° at 13 mm; n_D^{20} 1.5108 [14].

Acetylation of furfuryl alcohol. By the same procedure, using 9.8 g (0.1 mole) furfuryl alcohol, 8.6 g (0.1 mole) vinyl acetate and 1.1 g(0.05 g-atom) sodium, 7.0 g furfuryl acetate was obtained. Yield about 50% of theoretical (98% reckoned on the alcoholate). B.p. 83-85° at 15 mm.

n_D^{20} 1.4662; d_4^{20} 1.1117; MR_D 34.89; calculated 34.69.

Literature data: b.p. 175-177°; d_4^{20} 1.1176 [15].

Preparation of vinyl benzoate. A mixture of 34.4 g (0.4 mole) vinyl acetate, 24.4 g (0.2 mole) benzoic acid, 0.4 g mercuric acetate and 2 drops sulfuric acid was heated with stirring for 24 hours at 45-50°. A suspension of 20 g sodium carbonate in 50 ml water was then added and the organic layer was separated. The ether was distilled off and the residue distilled in vacuum to give 11.9 g (41%) vinyl benzoate. B.p. 98-100° at 24 mm.

n_D^{20} 1.5282; d_4^{20} 1.0683; MR_D 42.65; calculated 41.34.

Literature data: b.p. 72-73° at 3 mm; n_D^{20} 1.5279; d_4^{20} 1.069 [8].

Preparation of vinyl butyrate. From 8.8 g butyric acid, 17.2 g vinyl acetate, 0.22 g mercuric acetate and 1 drop sulfuric acid, using the same procedure, was obtained 5.8 g (51%) vinyl butyrate. B.p. 115-116° at 774 mm.

n_D^{20} 1.4096; d_4^{20} 0.8966; MR_D 31.25; calculated 31.19.

Found %: C 63.14, 63.19; H 8.80, 8.87. $C_6H_{10}O_2$. Calculated %: C 63.21; H 8.84.

Reaction of aniline with vinyl benzoate. To a mixture of 2.3 g (0.025 mole) aniline and 3.7 g (0.025 mole) vinyl benzoate was added 2 drops concentrated sulfuric acid. After the spontaneous heating had ceased, the mixture was heated for 30 minutes to 100-120°; the cooled mixture crystallized. The reaction product was pulverized, washed with hydrochloric acid and recrystallized from alcohol. Yield 3.5 g (71%) benzanilide. M.p. 160-161° in agreement with the literature.

Similarly (but without addition of sulfuric acid), 2.8 g aniline and 3.7 g vinyl butyrate gave 4.0 g (82%) butyranilide. M.p. 92° in agreement with the literature.

SUMMARY

1. The acylation is described of alcohols with the help of vinyl acetate which proceeds both in an acidic and an alkaline medium. A mechanism for the reaction is proposed.

2. The employment of vinyl esters of other acids as acylating agents is demonstrated with reference to the acylation of aniline with vinyl benzoate and vinyl butyrate.

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* See Consultants Bureau Translations, page 779.

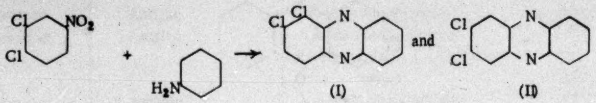
SYNTHESIS OF HALOGEN DERIVATIVES OF PHENAZINE

II. DICHLOROPHENAZINES

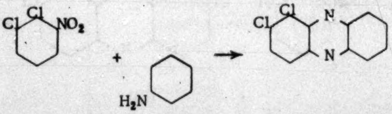
V. P. Chernetsky and A. I. Kiprianov

In the previous communication [1], the synthesis was described of mono- and dichlorophenazines by alkaline condensation of chloronitrobenzenes with aniline and chloroanilines *. In the present paper we describe the synthesis and properties of five new bases: 1,2-, 1,3-, 1,4-, 2-3- and 2,7-dichlorophenazines, and some of their N-oxides. We thus now know all ten of the possible isomers of dichlorophenazine. In this paper are also described the 4 isomeric dichloronitrodiphenylamines, which we prepared at the same time as the above-enumerated phenazines.

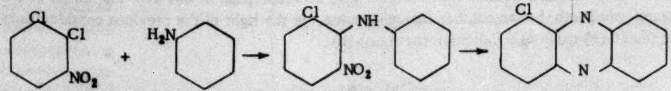
The synthesis and proof of structure of the new dichlorophenazines were carried out by the following methods. 1,2-Dichlorophenzine was prepared by condensation of 3,4-dichloronitrobenzene [3] with aniline in presence of powdered KOH. As we see from the reaction scheme



the formation is possible of a mixture of two isomers (I) and (II). Chromatographic treatment of the reaction products yielded only one light-yellow base with m.p. 175-177° and one bright-yellow N-oxide which melted with decomposition at 217-219°. Reduction of the N-oxide with tin chloride in hydrochloric acid gave the same dichlorophenazine with m.p. 175-177°. In order to solve the problem of the structure of this base, we performed the alkaline condensation of 2,3-dichloronitrobenzene with aniline, which we assumed must lead only to 1,2-dichlorophenazine



The resultant phenazine derivative, however, melted at 120-122° and did not give a depression with 1-chlorophenazine. Evidently the mobile chlorine atom in the 2-position had split off in the first stage of the condensation



Dichlorophenazine could not be detected among the products of this experiment.

We then investigated the condensation of 3,4-dichloroaniline with nitrobenzene. Here the possibility of loss of a chlorine atom was excluded and the formation was to be expected of the very same isomeric dichlorophenazines (I) and (II) as in the first condensation. Actually in this case, again, only one dichlorophenazine was obtained, but it differed from the first in having a much higher (250-251°) melting point. The different melting points alone suffice to indicate that the isomer with the higher melting point has the more symmetrical structure (II) and the one with the lower melting point the less symmetrical structure (I). The structure of the base with m.p. 250-251° was conclusively established by its transformation into the dihydroxy derivative and then into the diacetoxy derivative with m.p. 239-240°. A diacetoxy derivative with the same melting point was obtained from 2,3-dihydroxy-

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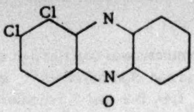
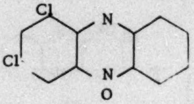
* After the present paper had gone to press, a paper appeared which described the synthesis of 1,5-dichlorophenazine by the same method [2].

phenazine which in turn was prepared from 2,3-diaminophenazine by the method of Fischer and Hepp [4]. A mixed test with both diacetyl derivatives did not give a depression. It was thus proved that the base with m.p. 250-251° is 2,3-dichlorophenazine; consequently, its isomer with m.p. 175-177° is 1,2-dichlorophenazine; the N-oxide with m.p. 217-219° (with decomposition), obtained in the first condensation, was evidently the oxide of 1,2-dichlorophenazine. We did not establish the actual position of the oxygen atom in this and the subsequently described N-oxides. In a paper by Pushkareva and Agibalova [5], and later in one by Pachter and Kloetzel [2], it was shown that the NO group in N-oxides of phenazines is formed on alkaline condensation of amines with nitro compounds at the expense of the nitro group. Consequently, in our case, the 10-(N)-oxide of 1,2-dichlorophenazine (a) was obtained. 1,3-Dichlorophenazine was isolated by condensation of 3,5-dichloronitrobenzene [6] with aniline.



(a)

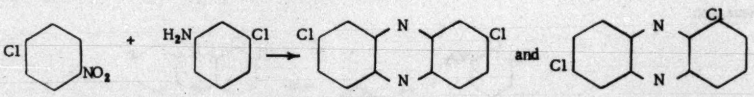
Chromatographic separation of the condensation products on alumina gave, apart from the base, its N-oxide, to which in accordance with the above considerations, we must ascribe the structure of the 10-(N)-oxide of 1,3-dichlorophenazine (b)



(b)

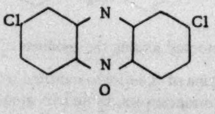
1,4-Dichlorophenazine was synthesized by condensation of 2,5-dichloronitrobenzene with aniline.

Alkaline condensation of p-nitrochlorobenzene with m-chloroaniline could yield two isomeric dichlorophenazines: 1,6- and 2,7-dichlorophenazines (IV) and (III)



(III) (IV)

1,6-Dichlorophenazine (IV) with m.p. 171-173° was prepared by us previously [1]. The above condensation scheme yielded only one dichlorophenazine with m.p. 229-230° which was consequently 2,7-dichlorophenazine (III). A yellow N-oxide was also isolated which melted with decomposition at 232-233° and on reduction with tin chloride was transformed into the same 2,7-dichlorophenazine. In the light of the previous considerations, this N-oxide must be the 10-(N)-oxide of 2,7-dichlorophenazine (c)



(c)

In Table 1 are listed the mono- and dichlorophenazines which we prepared by alkaline condensation, together with the starting materials and yields.

The yields set forth in Table 1 are not optimum. There is no doubt that the yields could be raised by suitable choice of conditions of condensation for each individual derivative. It is noteworthy that N-oxides are only formed in those cases where a chlorine atom is not adjacent to the NO group.

TABLE 1

Starting compounds		Chlorophenazines obtained	Yield in % of theory	
Nitro compound	Amine		Of individual compounds	Total
o-Nitrochlorobenzene	Aniline	1-Chlorophenazine	12.4	
	o-Chloroaniline	1,5-Dichlorophenazine	8.1	
	m-Chloroaniline	1,6-Dichlorophenazine	10.4	26.8
		1,8-Dichlorophenazine	16.4	
	p-Chloroaniline	1,7-Dichlorophenazine	10.5	
p-Nitrochlorobenzene	Aniline	10-(N)-oxide of 2-chlorophenazine	16	
	m-Chloroaniline	2,7-Dichlorophenazine	11.4	13.9
		10-(N)-oxide of 2,7-dichlorophenazine	2.5	
	p-Chloroaniline	10-(N)-oxide of 2,6-dichlorophenazine	17	
Nitrobenzene	3,4-Dichloroaniline	2,3-Dichlorophenazine	2	
2,3-Dichloronitrobenzene	Aniline	1-Chlorophenazine	6	
2,5-Dichloronitrobenzene	Aniline	1,4-Dichlorophenazine	24	
3,4-Dichloronitrobenzene	Aniline	1,2-Dichlorophenazine	6.8	17
		10-(N)-oxide of 1,2-dichlorophenazine	10.2	
3,5-Dichloronitrobenzene	Aniline	1,3-Dichlorophenazine	10.0	21
		10-(N)-oxide of 1,3-dichlorophenazine	11.0	

In Table 2 are listed the 12 possible mono- and dinitrophenazines and their melting points.

TABLE 2

Chlorophenazines	M.p.	Literature
1-Chlorophenazine	122-123	Wrede and Mülroth [7]
2-Chlorophenazine	140-141	McCombie et. al., [8]
1,2-Dichlorophenazine	175-177	V. P. Chernetsky and A. I. Kiprianov*
1,3-Dichlorophenazine	191-192	
1,4-Dichlorophenazine	198-199	
1,5-Dichlorophenazine	271-272	V. P. Chernetsky, S. B. Serebryany [1]; Pachter and Kloetzel [2]
1,6-Dichlorophenazine	171-173	V. P. Chernetsky [1]
1,7-Dichlorophenazine	222-223	
1,8-Dichlorophenazine	211-212	
2,3-Dichlorophenazine	250-251	V. P. Chernetsky and A. I. Kiprianov*
2,6-Dichlorophenazine	266-267	Bamberger, Ham [9]
2,7-Dichlorophenazine	227-228	V. P. Chernetsky and A. I. Kiprianov*

Omitted from Table 2 is the dichlorophenazine with m.p. 144° described by Claus in 1875 [10]. Claus had evidently obtained a mixture of isomers which he failed to resolve.

As indicated at the start of the present communication, several dichloronitrodiphenylamines were isolated from the products of alkaline condensation. Condensation of 3,4-dichloroaniline with nitrobenzene gave, apart from 2,3-dichlorophenazine, two isomeric dichloronitrodiphenylamines – reddish-orange with m.p. 161-162° and yellow with m.p. 214-215°. Formation of derivatives of diphenylamine in the alkaline condensation of nitro compounds with amines must clearly be regarded as the first stage in the synthesis of phenazines

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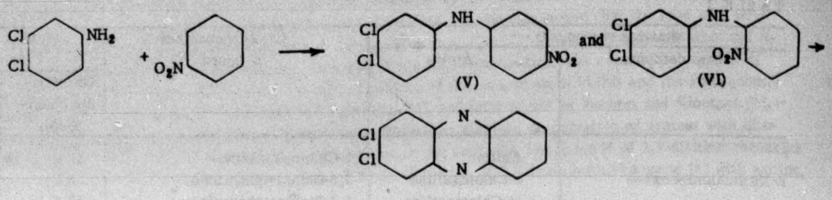
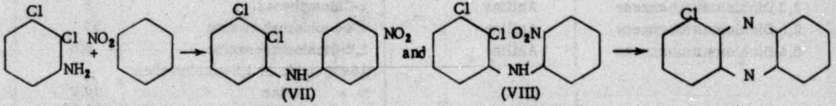
* See this paper



The more deeply colored product with m.p. 161-162° proved to be identical with 3,4-dichloro-2'-nitrodiphenylamine (VI), which we prepared by heating 3,4-dichloroaniline with o-nitrochlobenzene in presence of sodium acetate [11]. Consequently, we must ascribe the structure of 2,3-dichloro-4'-nitrodiphenylamine (V) to the yellow preparation with m.p. 214-215°.

Condensation of 2,3-dichloroaniline with nitrobenzene was also performed. This condensation proceeded with displacement of an atom of chlorine and gave 1-chlorophenazine. From the reaction products were isolated two isomeric dichloronitrodiphenylamines, one of which was orange-red with m.p. 147-148°, and the other yellow with m.p. 156-157°. In accordance with the reaction scheme



and taking into account the fact that o-nitroamines are more deeply colored than p-nitroamines, we should ascribe to the preparation with m.p. 147-148° the constitution of 2,3-dichloro-2'-nitrodiphenylamine (VIII), and to the preparation with m.p. 156-157° the constitution of 2,3-dichloro-4'-nitrodiphenylamine (VII).

Small quantities of diphenylamine derivatives were formed in all our condensations. The yield of these secondary or intermediate products can be raised by introducing a 2- or 3-fold excess of nitro component into the alkaline condensation with the amine.

EXPERIMENTAL

The procedure used in this investigation for the condensation of aromatic nitro compounds with amines was the same as in the preceding communication with the sole difference that it was found possible to limit the duration of condensation to 3 hours without detriment to the yield. For purification of the reaction products, steam distillation from the alkaline mixture of the toluene and unreacted nitro and amino components was excluded because it was observed that the amount of resin increased on distillation in presence of alkali. At the conclusion of the heating, the toluene solution was filtered off and the alkaline residue extracted with small portions of boiling toluene. The solvent was driven off from the combined toluene solutions and the residue chromatographed on alumina. For the purpose of complete separation the chromatographic treatment from benzene, chloroform or dichloroethane solutions was repeated 2-3 times. The substances isolated by the chromatographic separation were recrystallized.

1-Chlorophenazine was prepared by condensation of 1.8 g 2,3-dichloronitrobenzene with 0.88 g aniline in presence of 3.7 g powdered KOH in 15 ml toluene. Yield 0.112 g (6% of the theoretical); pale-yellow needles from alcohol, m.p. 121-122°.

1,2-Dichlorophenazine was synthesized from 11.2 g 3,4-dichloronitrobenzene and 9.3 g aniline in 150 ml toluene in presence of 28.5 g powdered KOH. Chromatographic treatment of the chloroform solution and recrystallization from dichloroethane gave 168 g (6.8%) 1,2-dichlorophenazine in the form of clusters of light-yellow small needles, m.p. 175-177°.

Found %: N 11.08, 11.14; Cl 28.80, 28.77. $C_{12}H_6N_2Cl_2$. Calculated %: N 11.24; Cl 28.51.

10-(N)-oxide of 1,2-dichlorophenazine was obtained in the same experiment by chromatographing of the products. Long, bright-yellow needles from dichloroethane. Yield 2.7 g (10.2%), m.p. 217-219° (with decomposition).

Found %: N 10.59, 10.60; Cl 26.50. $C_{12}H_6ON_2Cl_2$. Calculated %: N 10.57; Cl 26.79.

2,3-Dichlorophenazine was prepared by heating a mixture of 32.4 g 3,4-dichloroaniline, 73.8 g nitrobenzene, 100 g powdered KOH and 300 ml toluene. Crystallization from dichloroethane gave 0.95 g (2%) light-yellow needles, m.p. 250-251°.

Found %: N 11.29, 11.37; Cl 28.57. $C_{12}H_6N_2Cl_2$. Calculated %: N 11.24; Cl 28.51.

1,3-Dichlorophenazine was prepared by heating a mixture of 19.2 g 3,5-dichloronitrobenzene, 9.3 g aniline, 28.5 g powdered KOH and 150 ml toluene. After chromatographing and crystallization from alcohol, there was obtained 2.5 g (10 %) pale-yellow, small needles, m.p. 191-192°.

Found %: N 11.11, 11.02; Cl 28.22. $C_{12}H_6N_2Cl_2$. Calculated %: N 11.24; Cl 28.51

1-(N)-oxide of 1,3-dichlorophenazine was obtained in the same experiment by chromatogramming of the products from dichloroethane. Crystallization gave 2.8 g (11%) bright-yellow, slender, small needles, m.p. 236-237° (with decomposition).

Found %: N 10.59, 10.71; Cl 26.43, 26.67. $C_{12}H_6ON_2Cl_2$. Calculated %: N 10.57; Cl 26.79.

1,4-Dichlorophenazine was prepared from 19.2 g 2,5-dichloronitrobenzene, 9.3 g aniline, 28.5 g powdered KOH and 150 ml toluene. Yield 6 g (24%). Long yellow needles (from dichloroethane), m.p. 198-199°.

Found %: N 11.02, 11.20; Cl 28.48, 28.85. $C_{12}H_6N_2Cl_2$. Calculated %: N 11.24; Cl 28.51.

2,7-Dichlorophenazine was prepared from 15.75 g p-nitrochlorobenzene, 12.8 g m-chloroaniline, 29 g pulverized KOH and 150 ml toluene. The solution in toluene was chromatogrammed. Yield 2.83 g (11.4%) base. Pale-yellow needles, m.p. 229-230° (from benzene).

Found %: N 11.33, 11.41; Cl 28.63, 28.59. $C_{12}H_6N_2Cl_2$. Calculated %: N 11.24; Cl 28.51.

10-(N)-oxide of 2,7-dichlorophenazine was obtained at the same time as the above base. Yield 0.61 g (2.5%). Crystallized from benzene as bright-yellow needles, m.p. 232-233° (with decomposition).

Found %: N 10.67, 10.71; Cl 26.55. $C_{12}H_6ON_2Cl_2$. Calculated %: N 10.57; Cl 26.79.

3,4-Dichloro-2'-nitrodiphenylamine was isolated during chromatogramming of the products in the preparation of 2,3-dichlorophenazine in amount of 4.3 g (7.5%). Red-orange needles from ligroine, m.p. 161-162°.

Found %: N 9.95, 10.10; Cl 24.85, 24.92. $C_{12}H_8O_2N_2Cl_2$. Calculated %: N 9.89; Cl 25.09.

The same compound was obtained by 20 hours' boiling of a mixture of 8.1 g 3,4-dichloroaniline, 7.9 g o-nitrochlorobenzene, 37 g nitrobenzene and 8.2 g potassium acetate. The nonreacted materials were distilled off in steam and the residue was recrystallized from aqueous alcohol. Yield 0.7 g (5%) red-orange needles, m.p. 158-159°. A mixed melting test with the preceding preparation did not give a depression.

3,4-Dichloro-4'-nitrodiphenylamine was isolated from the products in the synthesis of 2,3-dichlorophenazine. Yield 3.66 g (6.45%). Yellow-orange platelets from benzene, m.p. 214-215°.

Found %: N 10.08, 10.04; Cl 25.01, 25.11. $C_{12}H_8O_2N_2Cl_2$. Calculated %: N 9.89; Cl 25.09.

2,3-Dichloro-2'-nitrodiphenylamine was isolated from the products of condensation of 2.6 g 2,3-dichloroaniline, 6.85 g nitrobenzene and 95 g KOH powder in 30 ml toluene. 0.22 g (4.9%) orange-red needles from alcohol, m.p. 147-148°.

Found %: N 10.05, 9.79; Cl 24.85, 24.97. $C_{12}H_8O_2N_2Cl_2$. Calculated %: N 9.89; Cl 25.09.

2,3-Dichloro-4'-nitrodiphenylamine was isolated at the same time as the preceding preparation by chromatogramming from dichloroethane. 0.46 g (10.2%), bright-yellow needles from alcohol, m.p. 156-157°.

Found %: N 9.99, 10.13; Cl 25.09, 24.90. $C_{12}H_8O_2N_2Cl_2$. Calculated %: N 9.89; Cl 25.09.

SUMMARY

5 new bases were prepared by alkaline condensation of aromatic amines with nitro compounds: 1,2-, 1,3-, 1,4-, 2,3-, and 2,7-dichlorophenazines. The following N-oxides were isolated at the same time: 10-(N)-oxide of 1,2-dichlorophenazine, 10-(N)-oxide of 1,3-dichlorophenazine and 10-(N)-oxide of 2,7-dichlorophenazine.

Secondary and intermediate products of alkaline condensation which were isolated were 2,3- and 3,4-dichloro-2'-nitrodiphenylamines and 2,3- and 3,4-dichloro-4'-nitrodiphenylamines.

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CONFIGURATION AND PROPERTIES

OF UNSATURATED ACIDS AND THEIR DERIVATIVES

THE OXIDATION OF OCTADECENOIC ACIDS AND THEIR ESTERS

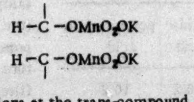
A. K. Plisov and N. P. Bulatsky

The structure of oleic acid was established by E. E. Vagner and was later confirmed by Baruch, although in contemporary literature, both at home and abroad, Baruch is credited with being the first to establish the correct formula of oleic acid [1]. However, this claim, which is accepted at the present time, does not correspond to reality. Actually, the first scientist who proposed the modern formula for oleic acid, in 1888, was the outstanding Russian chemist, Egor Egorovich Vagner [2]. Six years later, in 1894, Baruch [3] repeated the conclusions of E. E. Vagner and published his paper in the same journal in which Vagner's paper had appeared.

Concerning the spatial configuration of oleic acid, one of us has reported the data obtained on hydrogenation and oxidation of the geometrically isomeric octadecenoic acids [4]. Later Plisov and Maleeva studied the oxidation of oleic and elaidic acids with aqueous potassium permanganate [5] and showed that oleic and elaidic acids were oxidized at different velocities. Plisov and Bykovets made similar observations in respect of petroselinic and petroselaidic acids and their esters [10].

In these researches the reaction was performed at the surface between the acid or ester and an aqueous solution of the oxidizing agent. We considered that it was also necessary to clarify the nature of this reaction in a homogeneous medium.

We selected potassium permanganate as the oxidizing agent; it was used for the first time for the oxidation of oleic acid by Zaitsev [6]. The mechanism of this reaction which has been studied by many Russian chemists [7, 8], was clarified by Nametkin [9] and is considered to involve addition of the potassium permanganate at the double bond with formation of an unstable intermediate product:



$$\begin{array}{l} \phantom{H-{}}| \\ H-C-OMnO_2OK \\ H-C-OMnO_2OK \\ \phantom{H-{}}| \end{array}$$

We must assume that the spatial conditions at the trans-compound will to some extent hinder the formation of the indicated intermediate product.

As the solvent for this reaction, we selected acetone. This is convenient because after preliminary treatment with potassium permanganate, the acetone is oxidized extremely slowly; furthermore, we found that oxidation in acetone solution proceeds very much more slowly than in other solvents. This circumstance greatly facilitates the observations of changes in the rate of oxidation of oleic acid.

Since the blocking action of radicals at carbons linked by a double bond (steric hindrance) will mainly affect the first stage of the reaction (addition at the double bond), we decided to employ the oxidant in smaller quantities than are necessary for addition at the double bond, and to use weak solutions of oxidant.

Below are set forth the results of oxidation with potassium permanganate in acetone solution of oleic, elaidic, petroselinic and petroselaidic acids. As had been expected, the results demonstrate that the reactivity of these acids is consistent with the hypothesis of steric hindrance of the reactions, and they may serve as a basis for solution by a chemical method of the problem of the actual configuration of geometrically isomeric unsaturated acids.

EXPERIMENTAL

Pure oleic (9,10-octadecenoic) acid was obtained from commercial oleic acid via the lithium salts and had the following constants: b.p. 202° (5 mm); m.p. 14.4°; iodine number (Hübl) 90.04.

Elaidic acid was prepared by elaidinization of oleic acid and had the following constants after three recrystallizations from ethyl alcohol: b.p. 204° (5 mm); m.p. 51°; iodine number (Hübl) 89.96.

Petroselinic (6,7-octadecenoic) acid with m.p. 32.5° and iodine number 90.0 was isolated from coriander oil; its geometrical isomer (petroselaidic acid) was prepared by isomerization of petroselinic acid in presence of selenium and had, after recrystallization, m.p. 54° and iodine number 90.1.

The oxidation reaction was studied in a water thermostat in which the temperature could be kept constant to ± 0.05°. Comparable results were ensured by using identical weights of the acids concerned in two small flasks. To these was added acetone in quantity required to give a total volume of 2 ml in each flask (i.e., acid + acetone). The flasks were placed in the thermostat and after they had reached the temperature of the thermostat, addition was made of 48 ml oxidant solution. At specific intervals of time, 5 ml samples were withdrawn and the amount of unreacted oxidant was determined by titration of the reaction mixture with 0.04 N thiosulfate solution. Each experiment was repeated twice; the titration results varied by 0.02-0.04 ml.

TABLE 1

Experimental temperature 20°. Weight of acids 0.3115 g
Initial concentration of oxidant 0.04102 N.

Duration of oxidation (in minutes)	Amount of thiosulfate (in ml)			
	oleic acid	petroselinic acid	elaidic acid	petroselaidic acid
0	8.2	8.2	8.2	8.2
15	6.4	6.4	7.0	7.4
30	4.8	4.7	5.8	5.9
45	3.5	3.6	4.4	4.6
60	2.2	2.1	3.2	3.4
75	1.2	1.2	2.0	2.3
90	0.3	0.4	0.8	1.2

TABLE 2

Experimental temperature 10°. Weight of acids 0.3115 g
Initial concentration of oxidant 0.04102 N.

Duration of oxidation (in minutes)	Amount of thiosulfate (in ml)			
	oleic acid	petroselinic acid	elaidic acid	petroselaidic acid
0	8.2	8.2	8.2	8.2
30	6.7	6.7	7.3	7.4
60	5.4	5.3	6.4	6.8
90	4.2	4.4	5.4	5.9
120	3.2	3.4	4.3	4.8
150	1.9	1.9	3.4	4.0
180	0.5	0.6	2.5	3.0

TABLE 3

Experimental temperature 20°. Weight of acids 0.156 g.
Initial concentration of oxidant 0.04386 N.

Duration of oxidation (in minutes)	Amount of thiosulfate (in ml)			
	oleic acid	petroselinic acid	elaidic acid	petroselaidic acid
0	10.2	10.2	10.2	10.2
15	8.2	8.2	8.6	8.5
30	6.6	6.4	7.0	7.4
45	5.4	5.5	5.9	5.9
60	4.6	4.8	5.0	5.2
75	3.4	3.5	4.1	4.4
90	2.8	2.6	3.4	4.2

Since manganese dioxide is separated in the oxidation reaction and might obscure the titration data, we employed a method of sample withdrawal in vacuum which ensured manganese dioxide-free samples. For this purpose we used a tube to one end (the broad one) of which was attached a sintered porous plate. The required amount of reaction mixture was sucked into the tube with a pump and was filtered from manganese dioxide during this operation.

SUMMARY

1. Oleic and petroselinic acids are oxidized by potassium permanganate in acetone solution more rapidly than elaidic and petroselaidic acids.

2. Oxidation of octadecenoic acids with potassium permanganate in acetone solution proceeds as would be expected from the theory of steric hindrance.

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** " " " " " 637.

QUINONES

V. CHLORINATION OF 2,5-DIMETHOXYQUINONE

I. S. Ioffe and A. F. Sukhina

In continuation of previously described work [1] on the chlorination of methoxyquinone, we decided to study the chlorination of 2,5-dimethoxyquinone (I). The sole chloro derivative described in the literature, 3,6-dichloro-2,5-dimethoxyquinone (II), was prepared not by direct chlorination of dimethoxyquinone but indirectly either by methoxylation of tetrachloroquinone [2] or by methylation of potassium chloranilate [3].

2,5-Dimethoxyquinone dissolves readily only in heated nitrobenzene. In our first experiments, therefore, we passed chlorine through a nitrobenzene solution of 2,5-dimethoxyquinone heated on a boiling water bath. After driving off the solvent in vacuum and recrystallizing the residue from alcohol, we obtained the reaction product in the form of bright orange-red plates with m.p. 142°. This substance was found to be identical with the above-noted 3,6-dichloro-2,5-dimethoxyquinone.

Subsequently, we carried out the reaction of chlorine with 2,5-dimethoxyquinone in milder conditions, the stream of dry chlorine being passed through a cooled suspension of the quinone in chloroform. Although 2,5-dimethoxyquinone is insoluble in chloroform, with continued passage of chlorine it dissolves. By observing a series of precautions, using thoroughly dried chloroform and chlorine, we obtained an almost completely colorless solution containing —as further examination revealed —previously undescribed products of addition of chlorine to 2,5-dimethoxyquinone in the form of 2,5-dimethoxyquinone dichloride (III) and 2,5-dimethoxyquinone tetrachloride (IV).

In order to obtain 2,5-dimethoxyquinone dichloride, it is best to conduct the reaction so that a little of the original quinone remains in the reaction medium. If this procedure is not followed, 2,5-dimethoxyquinone dichloride is extremely difficult to purify from tetrachloride and its accompanying secondary products, which form a resinous oil in the mixture; it is easily freed from unreacted 2,5-dimethoxyquinone by filtration. 2,5-Dimethoxyquinone dichloride crystallizes from ligroine in colorless needles melting at 145° (with decomposition).

In order to obtain 2,5-dimethoxyquinone tetrachloride, which generally has poor stability, it is best to start from previously isolated dichloride; chlorine is passed through a cooled solution of the latter in chloroform. The tetrachloride is then obtained in the solid state and is purified by crystallization from ligroine; the resultant crystals are unstable when heated and melt with decomposition.

When studying the properties of methoxyquinone dichloride [1], it was established that the presence of the methoxy group lowers the stability of the corresponding quinone chlorides. This observation was confirmed in a study of the properties of 2,5-dimethoxyquinone dichloride (III) and tetrachloride (IV). Both of these compounds also have poor stability and readily lose hydrogen chloride to form the corresponding chloro derivatives of 2,5-dimethoxyquinone.

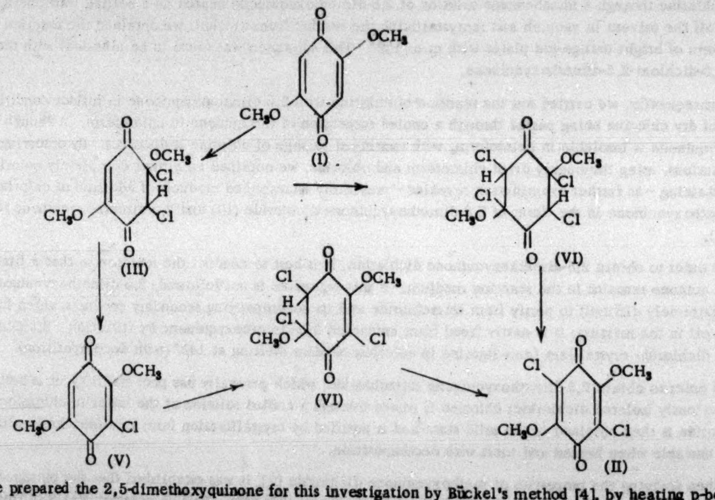
From the dichloride (II) is also obtained the undescribed 3-chloro-2,5-dimethoxyquinone (V), while the tetrachloride (IV) gives the already known 3,6-dichloro-2,5-dimethoxyquinone (II). 2,5-Dimethoxyquinone tetrachloride slowly loses hydrogen chloride even on keeping or on solution in alcohol without heating. Both chlorides quickly split off hydrogen chloride when melted; the most convenient way of transforming 2,5-dimethoxyquinone chlorides into the corresponding chloro derivatives of 2,5-dimethoxyquinone is by short-period heating of their alcoholic solutions. On cooling the latter, the chloro derivatives come down in the pure form: 3-chloro-2,5-dimethoxyquinone (V) in the form of light-yellow needles with m.p. 118-119°, and 3,6-dichloro-2,5-dimethoxyquinone (II) in the form of orange red platelets with m.p. 142°. The difference between the crystals is so great that these substances can be readily distinguished by their outward appearance, especially under the microscope. We exploited this difference in controlling the reaction during preparation of the tetrachloride.

3,6-Dichloro-2,5-dimethoxyquinone is rather less soluble in alcohol than the monochloro derivative. This difference can be utilized for the simultaneous preparation of both substances: a mixture of 2,5-dimethoxyquinone dichloride and tetrachloride is first prepared and then heated in alcohol; finally it is subjected to fractional crystallization.

3,6-Dichloro-2,5-dimethoxyquinone (II) was also prepared by us from previously isolated monochloro derivative (V), both directly and via the product of addition of chlorine to the latter, 3-chloro-2,5-dimethoxyquinone dichloride (VI). This compound is interesting because it contains one atom of chlorine replacing an atom of hydrogen and two atoms of chlorine added at the double bond of the quinoid nucleus. This addition product, obtained by passing chlorine through a solution of 3-chloro-2,5-dimethoxyquinone in chloroform, consisted of a light-colored oil which only solidified when cooled below −20°. This oil is soluble in boiling ligroine but on cooling, it separates out in the same form.

3-Chloro-2,5-dimethoxyquinone dichloride is extremely unstable and splits off hydrogen chloride even when kept. For this reason analytical determinations of the chlorine gave rather low results compared with the theoretical value. In alcoholic solution, especially when heated, the compound readily changes into 3,6-dichloro-2,5-dimethoxyquinone (II).

The transformations of the products of interaction of 2,5-dimethoxyquinone with chlorine which we studied are represented in the following scheme:



We prepared the 2,5-dimethoxyquinone for this investigation by Bückel's method [4], by heating p-benzoquinone with methyl alcohol in presence of zinc chloride. This reaction proceeds very smoothly, but the yield of 2,5-dimethoxyquinone reaches only 33% of the theoretical, reckoned on the quinone brought into reaction. According to Bückel, this low yield is due to initial formation of a product of addition of methyl alcohol to the quinone which rearranges into the corresponding methoxyhydroquinone and is oxidized by the quinone present to methoxyquinone.

The mechanism of this reaction has not yet been studied. It may be conjectured that it proceeds in several stages with intermediate formation of methoxyquinone, followed by an analogous transformation of the latter into 2,5-dimethoxyquinone. On this basis we hoped to raise the yield of 2,5-dimethoxyquinone by starting from previously prepared methoxyquinone. However, on heating methoxyquinone with methyl alcohol in presence of zinc chloride, we obtained no 2,5-dimethoxyquinone at all. It was found that in these conditions, under the influence of acid (formed by hydrolysis of the zinc chloride), the methoxyquinone undergoes transformation with formation of the product of condensation of two molecules described in the preceding communication. It follows from this that methoxyquinone cannot be regarded as an intermediate product in the preparation of 2,5-dimethoxyquinone by Bückel's reaction. It is more probable, as was suggested by the author himself, that in this reaction, more rapid formation occurs (according to the usual mechanism for quinones) of the product of addition of 2 molecules of methyl alcohol to a molecule of quinone, and this is oxidized to 2,5-dimethoxyquinone with excess of quinone. If this hypothesis is correct, then the formation of 1 molecule of 2,5-dimethoxyquinone would actually require 3 molecules of quinone and the yield of 2,5-dimethoxyquinone cannot exceed 33% of the theoretical. Since the dimethoxyquinone is completely insoluble in alcohol, it is continuously precipitated as formed.

We hoped to raise the yield of 2,5-dimethoxyquinone by adding to the solution various oxidants such as iron chloride or nitric acid. But in such cases the yield was actually lowered, probably due to breakdown of the addition product formed.

We also prepared 2,5-dimethoxyquinone by treatment with methanol of monochloroquinone in presence of zinc chloride. In such a case direct methoxylation is accompanied by unusually easy removal of the chlorine atom of the other methoxy group. This behavior confirms the above-described mechanism of the reaction. In the case, however, of the chloroquinone in the intermediately formed addition product, cleavage of hydrogen chloride and oxidation are possible at the same time.

EXPERIMENTAL

1) Dimethoxyquinone Dichloride

6 g 2,5-dimethoxyquinone is finely pulverized and brought into 80 ml dry chloroform. A stream of dry chlorine is passed through the suspension until nearly the whole of the dimethoxyquinone has entered into reaction and gone into solution. It is desirable to stop the flow of chlorine when there is still a little of the original quinone, since otherwise the tetrachloride is also formed. The resultant light-yellow solution is evaporated to a small bulk in vacuum. White crystals come down in the yellow oil. These are filtered, well pressed to remove oil, and washed with a little chloroform. The chloroform filtrate is diluted with ligroine, the precipitate is added to the main mass and the mixture is washed on the filter with ligroine.

The precipitate is purified by introducing it in small portions into boiling ligroine and then cooling the saturated solution. The resultant white crystals are filtered from the still-warm suspension. The whole of this operation must be performed quickly with avoidance of prolonged heating and prolonged standing of the solution. By adhering to these conditions, the reaction product is obtained in the pure form and is finally purified by one more recrystallization from ligroine. The yield of this product is about 4 g. Colorless, transparent needles melting at 145° (with decomposition). When heated with alcohol it splits off hydrogen chloride and forms 3-chloro-2,5-dimethoxyquinone. It is relatively stable when heated in ligroine.

0.1190 g sub.: 0.1416 g AgCl. 0.1261 g sub.: 0.1505 g AgCl. 0.1431 g sub.: 0.2807 g AgI. 0.1360 g sub.: 0.2688 g AgI. Found %: Cl 29.46, 29.52; OCH_3 25.87; 25.92. $C_6H_2O_2Cl_2(OCH_3)_2$. Calculated %: Cl 29.57; OCH_3 25.98.

2. Dimethoxyquinone Tetrachloride

2 g dimethoxyquinone dichloride is dissolved in 20 ml dry chloroform and a stream of chlorine is passed through the solution until a sample is found completely free from the original dichloride. The test is performed in the following manner: A few drops of solution are withdrawn from the reaction medium and put into 2 ml pure alcohol. The solution is brought to the boil and then cooled; the precipitate is transferred to the object glass of a microscope. The presence of long, acicular crystals of 3-chloro-2,5-dimethoxyquinone is evidence of the presence in the reaction medium of dichloride which has not yet entered into reaction. In the absence of the latter, only orange plates of 3,6-dichloro-2,5-dimethoxyquinone will be visible under the microscope; the latter is formed from the quinone tetrachloride.

When the test shows complete absence from the reaction medium of the original dichloride, the chloroform is distilled off in vacuum and the precipitate is washed with a little chloroform to remove the impurity in the form of a white mass. The crystaline precipitate is crystallized from ligroine with observance of the same precautions as for the crystallization of the dichloride.

Colorless crystals melting with decomposition. Dimethoxyquinone tetrachloride is less stable than the dichloride. On standing it slowly loses hydrogen chloride and is transformed into 3,6-dichloro-2,5-dimethoxyquinone. This transformation takes place very rapidly when the tetrachloride is put into boiling alcohol.

0.1362 g sub.: 0.2504 g AgCl. 0.1215 g sub.: 0.2238 g AgCl. 0.1574 g sub.: 0.2357 g AgI. 0.1214 g sub:

0.1835 g AgI. Found %: Cl 45.54, 45.61; OCH_3 19.74, 19.88. $C_6H_2O_2Cl_4(OCH_3)_2$. Calculated %: Cl 45.80; OCH_3 20.00.

3. 3-Chloro-2,5-dimethoxyquinone

3 g 2,5-dimethoxyquinone dichloride in small portions is introduced into 40 ml alcohol heated to the boil and the solution is boiled for 15 minutes. The reaction proceeds with evolution of hydrogen chloride. The solution gradually turns yellow and after cooling deposits light-yellow crystals of 3-chloro-2,5-dimethoxyquinone, which is purified by repeated crystallization from alcohol. Yield 3 g or 80% of the theoretically possible. Long light-yellow needles, m.p. 118-119°. Very slightly soluble in water; soluble in alcohol, ether, chloroform, gasoline and hot ligroine.

0.1198 g sub.: 0.0861 g AgCl. 0.1532 g sub.: 0.1090 g AgCl. 0.1004 g sub.: 0.2327 g AgI. 0.1384 g sub.: 0.3220 g AgI. Found %: Cl 17.79, 17.58; OCH_3 30.77, 30.72. $C_6HO_2Cl(OCH_3)_2$. Calculated %: Cl 17.53; OCH_3 30.62.

4. 3-Chloro-2,5-dimethoxyquinone Dichloride

3 g 3-chloro-2,5-dimethoxyquinone is dissolved in 30 g chloroform, the solution is cooled to 0°, and through it is passed chlorine until a test, similar to that described above for the preparation of 2,5-dimethoxyquinone tetrachloride, shows the complete absence of the original monochloro derivative from the reaction medium. The chloroform is then distilled off in vacuum and the residual yellow oil dissolved in boiling ligroine. On cooling, the reaction product separates in the form of heavy, oily drops which could not be crystallized after further purification. It only solidifies when cooled below −20°, but at 0° it again becomes oily. The color of the oil is light-yellow. On keeping, it slowly splits off hydrogen chloride and is transformed into 3,6-dichloro-2,5-dimethoxyquinone. In hot alcohol it quickly loses hydrogen chloride. It partly decomposes also when purified from ligroine and the chlorine content is, therefore, slightly lower than the theoretical value.

0.1542 g sub.: 0.2338 g AgCl. 0.1643 g sub.: 0.2512 g AgCl. Found %: Cl 37.52, 37.80. $C_8H_7O_4Cl_3$. Calculated %: Cl 38.93.

5. 3,6-Dichloro-2,5-dimethoxyquinone

a) 6 g 2,5-dimethoxyquinone is stirred into 60 ml nitrobenzene and the mixture is heated on a boiling water bath. Through this heated solution is passed a stream of dry chlorine for 2 hours. At the conclusion of the reaction, the nitrobenzene is taken off in vacuum and the dry residue crystallized from alcohol. Yield 6 g or 80% of the theoretical.

b) 3 g dimethoxyquinone tetrachloride is introduced into 40 ml boiling alcohol and boiling is continued for 15 minutes. The reaction is accompanied by evolution of hydrogen chloride. On cooling, the orange-yellow solution deposits crystals of 3,6-dichloro-2,5-dimethoxyquinone.

c) 3,6-Dichloro-2,5-dimethoxyquinone can also be obtained from the crude product of exhaustive addition of chlorine to 2,5-dimethoxyquinone, or from 3-chloro-2,5-dimethoxyquinone chloride, or from the resinous mass remaining on crystallization of 2,5-dimethoxyquinone dichloride.

The product is in the form of bright orange-red plates with m.p. 142°; insoluble in water, soluble in alcohol and ether. Readily crystallizes from ligroine. Is less soluble than the monochloro derivative in alcohol, and this difference can be utilized for separation from the latter by fractional crystallization.

0.1262 g sub.: 0.1540 g AgCl. 0.1416 g sub.: 0.1710 g AgCl. 0.1266 g sub.: 0.2486 g AgI. 0.1152 g sub.: 0.2283 g AgI. Found %: Cl 30.21, 29.92; OCH_3 25.95, 26.21. $C_6O_2Cl_2(OCH_3)_2$. Calculated %: Cl 29.96; OCH_3 26.16.

SUMMARY

Passage of chlorine through a solution of 2,5-dimethoxquinone in chloroform leads to 2,5-dimethoxyquinone dichloride and 2,5-dimethoxyquinone tetrachloride. Both these compounds have poor stability and lose hydrogen chloride readily with formation, respectively, of 3-chloro-2,5-dimethoxyquinone and 3,6-dichloro-2,5-dimethoxyquinone.

From 3-chloro-2,5-dimethoxyquinone was obtained 3-chloro-2,5-dimethoxyquinone dichloride which, by cleavage of HCl is also transformed into 3,6-dichloro-2,5-dimethoxyquinone.

3,6-Dichloro-2,5-dimethoxyquinone may also be obtained directly from 2,5-dimethoxyquinone by chlorination in heated nitrobenzene solution.

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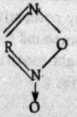
* See Consultants Bureau Translation, page 313.

NAPHTHOFUROXAN

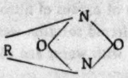
I. THE BISULFITE COMPOUND OF NAPHTHOFUROXAN

S. V. Bogdanov and B. I. Karavaev

As we know, oxidants act on the dioximes of o-quinones to form compounds with the general formula $R = N_2O_2$. These compounds are also obtained by oxidation of the corresponding o-nitroamino compounds or by decomposition of o-nitroazido compounds. These substances were formerly believed to have the structure of o-dinitroso compounds or of peroxides. Nowadays they are represented as oxides of furazines or as furoxans:



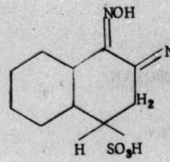
As evidence of the quinoid structure of these compounds, Hammick and others [1] adduce the addition of 4 atoms of bromine to benzofuroxan. The existence of two different products of oxidation of the amphi-dioximes of asymmetrical α-diketones, corresponding to the formulas of Meisenheimer and others [2], makes probable an asymmetrical configuration of the furoxan ring. Green and Rowe [4], who studied the oxidation of o-nitroanilines to the corresponding furoxans, at first proposed an asymmetrical formula for the latter and assumed that the nitrogen atom linked to the two oxygen atoms is located at the carbon previously linked with the nitro group. They later found, however, that oxidation of 4-chloro- and 5-chloro-2-nitroanilines leads to one and the same chlorobenzofuroxan [4]. A similar phenomenon is observed in the oxidation of 3-nitro-4-amino- or 4-nitro-3-aminotoluene and in the decomposition of 4- or 5-bromo-2-nitro-1-azidobenzene and 3-nitro-4-azido- or 4-nitro-3-azidotoluene [5]. Moreover, on oxidation of 2-nitro-1-naphthylamine and 1-nitro-2-naphthylamine and on decomposition of 2-nitro-1-azidonaphthalene or 1-nitro-2-azidonaphthalene, there is formed one and the same naphthofuroxan [6]. These facts led Green and Rowe to the conclusion that the furoxan group has the symmetrical structure



Although the attempt of Hammick and co-workers to establish the structure of furoxans by determination of the parachors of benzo- and methylbenzofuroxans did not lead to a decisive solution of the problem, they assumed an asymmetrical structure of furoxans. In their opinion, the formation of identical furoxans on oxidation of 4- or 5-substituted 2-nitroanilines is explained by the transition of the less stable furoxan isomer into the symmetrical o-dinitro form, followed by transformation into the stable isomer.

As previously pointed out [7], the sulfite compound of 1,2-naphthoquinone dioxime (I), which is obtained by the action of hydroxylamine on the bisulfite compound of 1-nitroso-2-naphthol, is converted by oxidation in an acidic medium into a colorless, crystalline substance containing nitrogen and sulfur. The oxidation product remained unexamined, but it was considered to be closely related to naphthofuroxan which was first prepared by Ilyinsky [8] by oxidation of 1,2-naphthoquinonedioxime. On resuming the study of some derivatives of 1-nitroso-2-naphthol, we repeated the experiments on oxidation of the sulfite of 1,2-naphthoquinonedioxime. Using nitric acid, nitrous acid and hydrogen peroxide, we obtained one and the same substance in which, judging by its reduction to 1,2-naphthylenediamine-4-sulfonic acid, the structure of the naphthalene ring is retained as well as the original position of the atoms of nitrogen and sulfur. We attributed to this compound the structure of the bisulfite compound of naphthofuroxan. Since no data are available about the linkages of the oxygen atoms in the nitrogen-containing naphthofuroxan ring, we consider it is expedient for the present to use the formula of Green and Rowe.

Some properties of the oxidation product will be described later, but here we describe its sodium, potassium, barium and benzidine salts.



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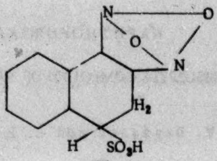

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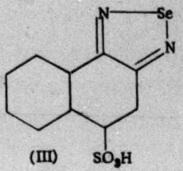

(III)

When preparing the initial sulfite compound of 1,2-naphthoquinonedioxime, it is unnecessary to boil the solution of the bisulfite compound of nitrosonaphthol with hydroxylamine (as indicated previously); the reaction already proceeds at room temperature, although much more slowly.

The structure of 1,2-naphthylenediamine-4-sulfonic acid was established by conversion with selenium dioxide into naphtho-selenoazole-sulfonic acid (III) and by comparison with the analogous product of transformation of the sulfonic acid prepared by cleavage of the azo compound formed from phenyldiazonium and 1-naphthylamine-4-sulfonic acid. In this case use was made with slight modification of Hinsberg's method [9] for the preparation of naphthoselenodiazole from 1,2-naphthylenediamine.

EXPERIMENTAL

Sulfite compound of 1,2-naphthoquinonedioxime was prepared by 30 minutes' boiling of a solution of the bisulfite compound of 1-nitroso-2-naphthol with a small excess of hydroxylamine hydrochloride and sodium acetate, followed by acidification of the cooled solution.

On standing a solution of 11.08 g of the bisulfite compound of 1-nitroso-2-naphthol, 6.53 g crystalline sodium acetate and 3.06 g hydroxylamine hydrochloride in 75 ml water at 18-20°, the reaction for 1-nitroso-2-naphthol disappeared after 48 hours. Acidification of the cooled solution with hydrochloric acid brought down 7 g of sulfite compound.

Oxidation of the Sulfite Compound

1. Nitric acid. To a solution of 10.8 g (0.04 mole) sulfite compound and 2.2 g crystalline sodium carbonate in 100 ml water was added 42.5 ml 59.4% nitric acid; the mixture was heated to 90-95° and kept at this temperature for 50 minutes. Already at 50° the evolution of oxides of nitrogen commenced and subsequently the odor of naphthofurazan was detected. Into the cooled and filtered solution was introduced 21 g crystalline sodium carbonate; the resultant precipitate was filtered and washed with water and alcohol. Yield 9.8 g.

The reaction may be so conducted that the stage of separation of sulfite compound is avoided. The paste of nitrosonaphthol, obtained in the usual way from 0.2 mole 2-naphthol, was washed until neutral and expressed; it was then dissolved in 57.4 g 36.2% sodium bisulfite diluted with an equal amount of water. Into the filtered solution was introduced 38 g crystalline sodium acetate and 16.8 g hydroxylamine hydrochloride; the solution was boiled for 30 minutes and filtered. After dilution to 260 ml, the filtrate was run over a period of $^1/_2$ hour into a heated (65-68°) solution of 164 ml 56.6% nitric acid in 200 ml water. The mixture was heated to 90°, kept at this temperature for 15 minutes and filtered. To the filtrate was added sodium chloride (20 g per 100 ml filtrate); the precipitated sodium salt of the oxidation product was filtered and washed with water and methyl alcohol. Yield 50.6 g (74% of theory on the 2-naphthol).

2. Nitrous acid. Into 90 ml solution of the bisulfite compound of 1,2-naphthoquinonedioxime, prepared from 0.1 mole 2-naphthol, was introduced 8 g sodium bicarbonate and 20.7 g sodium nitrite; the solution was run in the course of 35 minutes into a heated (30-40°) mixture of 40 ml 35.4% hydrochloric acid and 100 ml water. The suspension formed was heated to 95° and held at this temperature for 15 minutes. The solution was filtered and cooled. The precipitate was filtered and washed with water and methyl alcohol. Yield 19.0 g. Partial concentration of the filtrate led to separation of an additional 2.6 g substance.

3. Hydrogen peroxide. Into a boiling suspension of 5.4 g sulfite compound of 1,2-naphthoquinonedioxime in a mixture of 20 ml 35.4% hydrochloric acid and 40 ml water was run dropwise 30 ml 30% hydrogen peroxide. Fairly rapid formation occurred of a light-yellow solution containing an insignificant amount of resinous particles; the odor of chlorine was detected. The filtered and cooled solution was partly neutralized with sodium carbonate and the precipitate was filtered and washed with alcohol. Yield 2.5 g. The substance did not contain chlorine.

The same result was obtained by substituting sulfuric acid for hydrochloric acid.

The sodium salt of the product of oxidation was purified by crystallization from double the amount of water or by precipitation from an aqueous solution of alcohol. Colorless rectangular plates. Relatively stable in acid solutions, but boiling in 30-69% sulfuric acid resulted in browning and formation of naphthofurazan (m.p. 78°).

The compound contains 3 molecules of water of crystallization, 2¼ of which are driven off at 140°; at a higher temperature the compound decomposes.

0.1705 g sub.: 0.0352 g Na_2SO_4. 0.1416 g sub.: 10.2 ml N_2 (17°, 747 mm). Found %: Na 6.69; N 8.33. $C_{10}H_7O_5N_2SNa \cdot 3H_2O$. Calculated %: Na 6.69; N 8.14.

The potassium salt was prepared from the sodium salt. Colorless rectangular plates, fairly readily soluble in cold water, insoluble in alcohol.

1.1034 g sub.: loss on drying (130°) 0.0618 g. 0.0924 g sub.: 7.2 ml N_2 (21.5°, 729 mm). 0.2354 g dry sub.: 0.0648 g K_2SO_4. Found %: H_2O 5.60; N 8.66; K 12.35. $C_{10}H_7O_5N_2SK \cdot H_2O$. Calculated %: H_2O 5.55; N 8.64. $C_{10}H_7O_5N_2SK$. Calculated %: K 12.77.

The barium salt was prepared from the sodium salt. Colorless elongated plates with pointed ends; poorly soluble in cold and fairly soluble in hot water.

0.6954 g sub.: loss on drying (130°) 0.0914 g. 0.1275 g sub.: 0.0386 g $BaSO_4$. 0.0940 g sub.: 6.3 ml N_2 (20°, 748 mm). Found %: H_2O 13.12; Ba 17.81; N 7.68. $(C_{10}H_7O_5N_2S)_2Ba \cdot 5.5H_2O$. Calculated %: H_2O 12.85; Ba 17.82; N 7.27.

The benzidine salt was prepared from the sodium salt and benzidine hydrochloride. Colorless elongated plates, poorly soluble in cold and fairly soluble in hot water, insoluble in alcohol.

0.6132 g sub.: loss on drying (120°) 0.0290 g. 0.7374 g sub.: 19.71 ml 0.1 N $NaNO_2$. Found %: H_2O 4.73; M 748. $(C_{10}H_8O_5N_2S)_2C_{12}H_{12}N_2 \cdot 2H_2O$. Calculated %: H_2O 4.76; M 756.

1,2-Naphthylenediamine-4-sulfonic acid

1) To a solution of 20.6 g sodium salt of the bisulfite compound in 120 ml water is run in 120 ml ammonia solution, followed gradually at 33-50° by 40 g zinc dust. After 7 hours' stirring at 50°, the mixture is filtered and the filtrate acidified with hydrochloric acid. The precipitate is filtered and washed with water. Yield 9.1 g.

2) Into a solution of 10.3 g sodium salt in 150 ml water is run 35 ml 40% NaOH, followed at 15-35° over a period of 45 minutes by 20 g zinc dust. After 20 minutes' stirring at 35°, the mixture is filtered and the filtrate acidified with hydrochloric acid. The light-brown precipitate (prisms) is filtered and washed with water. Yield 6.8 g.

After reprecipitation from sodium acetate solution, the substance has a faint brown tint. Oxidation with nitric acid converts it into 1,2-naphthoquinone-4-sulfonic acid (characterized by formation of red 1,2-naphthoquinone-4-anilide with aniline), and treatment with the bisulfite compound of phenanthrenequinone gives naphthophenanthrazine-sulfonic acid (yellow needles, soluble in sulfuric acid with a blue color).

Naphthoselenodiazole-sulfonic Acid

Into a suspension of 7.14 g naphthylenediamine-sulfonic acid in 15 ml water was run 7.0 g selenium dioxide at the normal temperature in a single portion. After brief stirring, a brown solution was obtained. Into the solution was run 20 ml 34% NaOH and the light-colored precipitate was filtered and washed with water and alcohol. Yield 10.27 g.

The substance crystallized from water in the form of colorless long prisms.

1.0440 g sub.: loss on drying (130°) 0.0663 g. 0.3134 g dry sub.: 0.0651 g Na_2SO_4. Found %: H_2O 6.35; Na 6.73. $C_{10}H_5O_3N_2SSeNa \cdot 1.25\ H_2O$. Calculated %: H_2O 6.29. $C_{10}H_5O_3N_2SSeNa$. Calculated %: Na 6.86.

The sulfochloride was obtained by 48 hours' standing of a mixture of the sodium salt of the sulfonic acid with an equal amount of phosphorus pentachloride at the ordinary temperature and was separated by diluting the mixture with ice. Yellowish bipyramids (from chlorobenzene), m.p. 204.5-205.3°.

1,2-Naphthylenediamine-4-sulfonic acid, prepared by decomposition of the azo compound from phenyldiazonium and 1-naphthylamine-4-sulfonic acid, possessed the same properties as the product of reduction of the bisulfite compound. The sodium salt of naphthoselenodiazole-sulfonic acid was prepared as above.

1.0352 g sub.: loss on drying (130°) 0.0661 g. 0.1682 g dry sub.: 0.0352 g Na_2SO_4. Found %: H_2O 6.39; Na 6.78.

The sulfochloride had m.p. 205.5-206°; a mixture of both sulfochlorides melted at 205-205.5°.

SUMMARY

1. Oxidation of the sulfite of 1,2-naphthoquinonedioxime with nitric acid, nitrous acid or hydrogen peroxide leads to the sulfite of naphthofuroxan. The sodium, potassium, barium and benzidine salts of the oxidation product were prepared.

2. Reduction of the bisulfite compound of naphthofuroxan with zinc in presence of ammonia or sodium hydroxide leads to 1,2-naphthylenediamine-4-sulfonic acid.

3. Oxidation of 1,2-naphthylenediamine-4-sulfonic acid with selenium dioxide leads to naphthoselenodiazolesulfonic acid.

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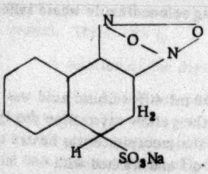
NAPHTHOFUROXAN

II. 2-NITRO-1-NAPHTHYLAMINO-4-SULFONIC ACID AND 2-NITRO-1-NAPHTHOL-4-SULFONIC ACID

S. V. Bogdanov and I. N. Koroleva

A method was previously described [1] for the preparation of the bisulfite compound of naphthofuroxan (I). This compound was found to be very unstable toward alkalies, the degree of sensitivity depending upon the conditions of use and the nature of the alkaline agent. Naphthofuroxan (II), the normal product of breakdown of the bisulfite compound, is formed only in minor amounts. Below is described the transformation of the bisulfite compound in presence of sodium carbonate.

Boiling of the bisulfite compound with sodium carbonate solution gives 2-nitro-1-naphthol-4-sulfonic acid (III), naphthofuroxan, naphthofurazan and a sulfonic acid of unknown structure, which contains nitrogen. In suitable conditions 2-nitro-1-naphthol-4-sulfonic acid is the main product of the reaction and is obtained in a yield of 93% of the theoretically possible. As experiments showed, the formation of this sulfonic acid proceeds via hydrolysis of the amino group in the initial reaction product – 2-nitro-1-naphthylamine-4-sulfonic acid (IV). This amino compound is obtained by keeping the bisulfite compound in 1% sodium carbonate solution at the ordinary temperature; heating greatly accelerates the reaction; after 10 minutes' boiling of this mixture the yield of 2-nitro-1-naphthylamine-4-sulfonic acid reaches 89% of the theoretical. Formation of secondary reaction products is also observed in this case.



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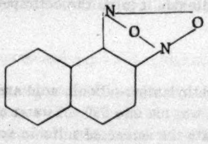

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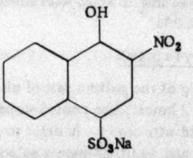

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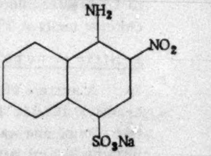

(IV)

Conversion of the bisulfite compound of naphthofuroxan into 2-nitro-1-naphthylamine-4-sulfonic acid is similar to some extent to the transformation of the bisulfite compound of 1-nitroso-2-naphthol into 1-amino-2-naphthol-4-sulfonic acid [2]. Naphthofuroxan is obtained as the result of normal decomposition of the bisulfite compound of naphthofuroxan, while the formation of naphthofurazan can be explained by reduction of naphthofuroxan and of the bisulfite compound of naphthofuroxan with the split-off sodium sulfite.

The structure of 2-nitro-1-naphthol-4-sulfonic acid was established by its conversion into 2,4-dinitro-1-naphthol, into 2-amino-1-naphthol-4-sulfonic acid and into 2-nitro-1-naphthol.

The structure of 2-nitro-1-naphthylamine-4-sulfonic acid, already inferred from its transformation into 2-nitro-1-naphthol-4-sulfonic acid, was confirmed by conversion into 1,2-naphthylenediamine-4-sulfonic acid and into 2-nitro-1-naphthylamine.

The diazo compound of 2-nitro-1-naphthylamine-4-sulfonic acid is obtained in normal conditions and possesses the normal azo-coupling ability; under the action of sodium carbonate, however, it loses the nitro group and is converted into the poorly active 1-diazo-2-naphthol-4-sulfonic acid.

EXPERIMENTAL

2-Nitro-1-naphthylamine-4-sulfonic Acid

1) Into a solution of 61.9 g (0.18 mole) sodium salt of the bisulfite compound of naphthofuroxan in 450 ml water is introduced at the ordinary temperature 4.5 g calcined sodium carbonate; the mixture is heated to the boil, and after 10 minutes' boiling it is cooled. The resultant very small yellowish precipitate, is filtered off and to the

filtrate is added sodium chloride (20% of the volume). The precipitated orange platelets of the sodium salt of nitronaphthylamine-sulfonic acid are filtered and washed with water, methyl alcohol and ether. Yield 46.75 g (89.5% of theory).

The filtrate and residue after evaporation of the alcohol and ether, is boiled for an hour. After cooling, the yellowish filtrate is filtered and washed with water. Weight of precipitate 1.86 g (precipitate a).

The filtrate is acidified with 8.5 ml hydrochloric acid and the resultant yellow crystalline precipitate is filtered and washed. Weight of substance 4.23 g (precipitate b).

2) To a solution of 10.3 g sodium salt of the bisulfite compound in 200 ml water was added 23 g 9.5% sodium carbonate solution and the mixture left for 18 hours at 18-20°. Addition of sodium carbonate to the filtered solution brought down 4.71 g sodium salt of nitronaphthylamine-sulfonic acid; boiling of the filtrate gave 0.28 g precipitate a and 2.23 g precipitate b.

The sodium salt is readily soluble in water and much less soluble in ethyl alcohol. From water it crystallizes in the form of orange, long, slender platelets. Drying at 125° indicated the absence of water of crystallization.

0.0994 g sub.: 0.0236 g Na_2SO_4. Found %: Na 7.69. $C_{10}H_7O_5N_2SNa$. Calculated %: Na 7.93.

The potassium salt (prepared from the sodium salt) crystallizes from water as orange prisms.

1.0028 g sub.: loss on drying (120°) 0.0494 g. 0.2066 g dry sub.: 0.0570 g K_2SO_4. Found %: H_2O 4.93; K 12.38. $C_{10}H_7O_5N_2SK \cdot H_2O$. Calculated %: H_2O 5.55. $C_{10}H_7O_5N_2SK$. Calculated %: K 12.77.

1,2-Naphthylenediamine-4-sulfonic Acid

Into a solution of 11.6 g sodium salt of the amino compound in 200 ml water, acidified with 64 ml hydrochloric acid, is introduced at 65-90° over a period of 40 minutes 16 g zinc dust, and the mass is stirred at 90° for another 20 minutes. The precipitate is filtered and washed with water. The yield of diamino compound, after reprecipitation from sodium acetate solution, is 7.1 g; long, slender prisms. With the bisulfite compound of phenanthrenequinone the substance gives the yellow naphthophenanthrazine-sulfonic acid; with nitric acid it is oxidized to 1,2-naphthoquinone-4-sulfonic acid; with selenium dioxide it forms the corresponding selenodiazole whose sulfochloride melts at 204.5-205°.

2-Nitro-1-naphthylamine

A mixture of 20 g of the sodium salt of nitronaphthylamine-sulfonic acid and 600 ml 40% sulfuric acid was heated at 108-112° for 2 hours. The cooled suspension was run into 800 ml water and the yellow crystalline precipitate filtered and washed with water. In order to separate the unreacted sulfonic acid, the precipitate was heated to 90° with 200 ml water and 40 ml ammonia solution, the insoluble portion was filtered off and washed with 400 ml water at 95°. Yield of nitronaphthylamine 6.23 g. (From the filtrates from the nitronaphthylamine was isolated 7.94 g potassium salt of the original sulfonic acid by addition of potassium chloride.) Nitronaphthylamine crystallizes from methyl alcohol as orange prisms with m.p. 142.5-143°. Nitrous acid converts it into a yellow solution of diazo compound which, with 2-naphthol-3,6-disulfonic acid, forms a blue-red dye and with resorcinol a reddish-brown dye. After treatment with sodium carbonate, the diazo compound does not couple with 2-naphthol-3,6-disulfonic acid, but with resorcinol it gives a lilac dye.

1-Diazo-2-naphthol-4-sulfonic Acid

A solution of 5 g of the sodium salt of nitronaphthylamine-sulfonic acid and 1.31 g sodium nitrite in 100 ml water is run over a period of 30 minutes at 3-7° into 10 ml hydrochloric acid + 100 ml water; the resultant suspension of diazo compound is stirred for another 1½ hours. The diazo compound (long, yellow prisms) gives, with 2-naphthol-3,6-disulfonic acid, a lilac dye, with resorcinol a brown dye, and with 2-naphthol-3,6-disulfonic acid a reddish-brown dye. To the suspension at 20° is added, over an hour, 8.5 g calcined sodium carbonate. The orange solution does not couple with the above-mentioned sulfonic acids, but with resorcinol it forms a deep lilac dye. The solution, after filtering from turbidity, is acidified with 25 ml hydrochloric acid. The precipitated diazonaphthol-sulfonic acid (yellow prisms) is filtered and washed to give 3.48 g (79.6%) diazo compound (64.3% of the theoretical amount).

The above-noted precipitate a was only partly soluble in hot water. From the aqueous solution were separated colorless prisms of sodium salt of the sulfonic acid. The compound was free from water of crystallization and contained 8% sodium. Reduction with zinc and hydrochloric acid converted it into 1,2-naphthylenediamine-4-sulfonic acid. The examination of the substance was not completed.

Recrystallization of the water-insoluble portion from methyl alcohol gave a small amount of naphthofurazan with m.p. 78° and a substance with m.p. 123.5-124.5°. The mixture of the substance with the naphthofuroxan obtained by oxidation of 1,2-naphthoquinonedioxime with nitric acid (m.p. 124.6-125.5°) melted at 124.5-125.5°.

Precipitate b was the sodium salt of 2-nitro-1-naphthol-4-sulfonic acid.

2-Nitro-1-naphthol-4-sulfonic Acid

1) A solution of 10 g sodium salt of nitronaphthylamine-sulfonic acid in 100 ml 14.1% sodium carbonate was boiled for 2 hours. The reddish-orange solution was diluted with 60 ml water and acidified with 30 ml hydrochloric acid; the precipitated sodium salt of nitronaphthol-sulfonic acid was filtered and washed with water. Yield 9.4 g or 88.2% of the theoretical.

2) To a boiling solution of 32 g calcined sodium carbonate in 150 ml water was added, over an hour, a solution of 20.6 g sodium salt of the bisulfite compound of naphthofuroxan in 150 ml water, and the boiling was continued for a further 2 hours. In the reflux condenser separated needles of naphthofurazan, while cooling of the solution brought out a mixture of secondary products (1.1 g) containing the same components as in precipitate a obtained during preparation of nitronaphthylamine-sulfonic acid. The filtrate from the precipitated sodium salt of nitronaphthol-sulfonic acid was filtered and washed. Yield 17.3 g (93.3% of the theoretical).

If solutions of bisulfite compound and sodium carbonate are mixed at the ordinary temperature and then heated, the yield of nitronaphthol-sulfonic acid falls while the amount of secondary products increases.

The sodium salt is fairly soluble in water, from which it crystallizes as yellow, slender platelets, difficultly soluble in alcohol.

1.0032 g sub.: loss on drying (125°) 0.0598 g. 0.0706 g dry sub.: 0.0168 g Na_2SO_4. Found %: H_2O 5.96; Na 7.70. $C_{10}H_6O_6NSNa \cdot H_2O$. Calculated %: H_2O 5.83. $C_{10}H_6O_6NSNa$. Calculated %: Na 7.90.

2-Amino-1-naphthol-4-sulfonic Acid

A solution of 4.4 g sodium salt of nitronaphthol-sulfonic acid in 150 ml water was boiled with a solution of tin chloride (150% excess) in hydrochloric acid for 20 minutes. The precipitate (long prisms) was filtered and washed. Yield 3.22 g.

A solution of the diazo compound gave a magenta-red coloration with resorcinol.

2.85 g amino compound was gradually brought at 5-10° into a mixture of 1.3 ml nitric acid (sp. gr. 1.35) and 3 ml water. The mass was diluted with water and to the filtered solution was added a saturated solution of potassium chloride; the precipitated potassium salt of 1,2-naphthoquinone-4-sulfonic acid was filtered; yield 2.36 g. Addition of an aqueous solution of aniline to the solution of potassium salt led to precipitation of 1,2-naphthoquinone-4-anilide. The compound crystallizes from alcohol in the form of small red needles, m.p. 257° (with decomposition).

2,4-Dinitro-1-naphthol

To a solution of 5 g nitronaphthol-sulfonic acid in 150 ml water was added 15 ml nitric acid (sp. gr. 1.35) and the mixture gradually heated to the boil. The dinitronaphthol formed was filtered and reprecipitated from sodium carbonate solution; yield 2.48 g. The compound crystallized from alcohol as yellow needles, m.p. 138.5° (with decomposition). (Formation of dinitronaphthol is facilitated by adding a small quantity of sodium nitrite to the solution of nitronaphthol-sulfonic acid.)

2-Nitro-1-naphthol

A mixture of 5 g nitronaphthol-sulfonic acid and 90 g 40% sulfuric acid was boiled for 7 hours. After only 30 minutes a sublimate of yellow needles of nitronaphthol had formed in the upper part of the flask. The mixture was diluted with water and the nitronaphthol filtered off; yield 2.1 g. The compound was reprecipitated from sodium carbonate solution and crystallized from methanol. Long yellow prisms, m.p. 128.5-129°.

SUMMARY

1. The main product of transformation of the bisulfite compound of naphthofuroxan in weak sodium carbonate solution at the ordinary temperature or after short-period boiling is 2-nitro-1-naphthylamine-4-sulfonic acid.

2. Prolonged boiling of the bisulfite compound with sodium carbonate solution leads mainly to formation of 2-nitro-1-naphthol-4-sulfonic acid.

3. Decomposition of the bisulfite compound of naphthofuroxan in sodium carbonate solution gives, apart from

2-nitro-1-naphthylamine-4-sulfonic acid and 2-nitro-1-naphthol-4-sulfonic acid, small amounts of naphthofuroxan and naphthofurazan.

4. The diazo compound of 2-nitro-1-naphthylamine-4-sulfonic acid is transformed by the action of sodium carbonate into 1-diazo-2-naphthol-4-sulfonic acid.

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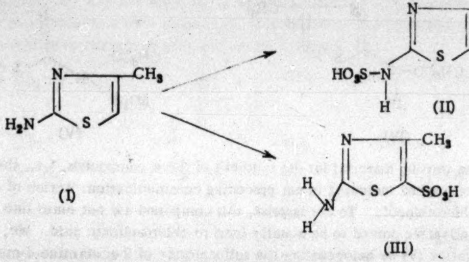
* See Consultants Bureau Translation, page 1855.

THE STRUCTURE OF THE SULFONIC ACIDS OF 2-AMINO-4-METHYLTHIAZOLE

I. Ya. Postovsky and T. S. Mamykina

On sulfonating 2-amino-4-methylthiazole (I), Ochiai and Nagasawa [1] obtained, depending on the reaction conditions, two isomeric acids: in the cold they obtained an acid with m.p. 256° (with decomposition), while with heating on the water bath they got an acid whose decomposition point was above 340°. The acid with m.p. 256° changes into the acid with decomposition point above 340° when heated with strong sulfuric acid. This transition of a low-melting sulfonic acid into a high-melting one is analogous to the known conversion of arylsulfamic acids into arylaminosulfonic acids. On this analogy, Ochiai and Nagasawa regarded the acid with m.p. 256° as a sulfamic acid and the one with m.p. above 340° as the 5-sulfonic acid.

In the present communication, we show that this argument "by analogy" is fallacious and that in the 2-aminothiazole series there occurs a characteristic transition in the reverse direction from the sulfonic acid (III) into the sulfamic acid (II).



We reached this conclusion on the basis of a repeated study of the structure of the sulfochloride and sulfamides of 2-acetamino-4-methylthiazole which we had previously described (IV) [2].

It was shown at the time that the action of chlorosulfonic acid on 2-acetamino-4-methylthiazole (IV) leads smoothly to the sulfochloride from which, by reaction with various amines, can be obtained a series of sulfamides. In order to establish the position of the sulfamido group, the starting sulfochloride was subjected to hydrolysis. This gave an acid with m.p. 253-255° (with decomposition) which, according to Ochiai and Nagasawa, should be regarded as the sulfamic acid. It was, therefore, concluded that in the chlorosulfonation of 2-acetamino-4-methylthiazole, the hydrogen of the acetamino group is substituted and that, consequently, the sulfamides are derivatives of the sulfamic acid (II).

Almost simultaneously with the publication of our paper in which these conclusions were announced, papers appeared by Backer and co-workers [3, 4] describing the sulfochloride of 2-acetamino-4-methylthiazole and the sulfamides prepared from this sulfochloride. The compounds described by Backer and co-workers, as far as can be judged from the melting points cited in the abstract of the paper [3], are identical with the compounds previously prepared by us. But Backer and co-workers regarded their compounds as derivatives of the sulfonic acid (III) without putting forward any experimental evidence in support of this assumption.

Two years later a detailed paper was published by Hurd and Kharasch [5] devoted to the structure of the sulfonic acids of Ochiai and Nagasawa. In it the authors arrived at the conclusion that the low-melting acid with m.p. 253° is the sulfamic acid, i.e., they supported the data of Ochiai and Nagasawa for the structure of the sulfonic acids of 2-amino-4-methylthiazole and their views on the isomerization of these acids.

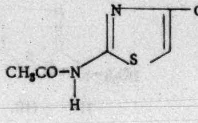
Although in the paper of Hurd and Kharasch no strict proof is advanced for the structure of the sulfonic acids of 2-amino-4-methylthiazole, their arguments in some measure confirmed our conclusion about the structure of the sulfochloride and the sulfamides as derivatives of the sulfamic acids (II). Later Hurd and Wehrmaster [6], in a reconsideration of the structure of the sulfochloride, pointed out the correctness of our conclusions about the structure of the sulfochloride, based on the results of hydrolysis of the sulfochloride to the acid with m.p. 253°. However, all these data conflicted with the observations according to which substitutions in 2-acetylamino-4-methylthiazole proceed easily in the 5-position (for example, halogenation and other reactions) [1, 7].

For these reasons, a number of authors still consider the question of the structure of the sulfochloride to be an open one [8].

For the purpose of verifying our conclusions about the structure of the sulfochloride prepared by the action of chlorosulfonic acid on 2-acetamino-4-methylthiazole, we thought it would be expedient to carry out the reverse conversion of the acid with m.p. 253°, prepared by Hurd and Kharasch, into the sulfochloride.

The acid with m.p. 253°, prepared (according to Hurd and Kharasch) by the action of strong sulfuric acid on free 2-amino-4-methylthiazole in dichloroethane solution, was converted into the sodium salt and acetylated by heating with acetic anhydride. Reaction of the acetyl derivative with PCl_5 gave an acid chloride whose properties and melting point (mixed test) proved to be identical with those of the sulfochloride obtained by us by direct chlorosulfonation of the acetyl derivative of amine (IV). In this manner the circle was completed, so to speak, of the transformations, which confirmed our previously enunciated conclusions on the structure of the sulfochloride.

Nevertheless, as we shall see later, in these conclusions resides an error which could only be revealed in the course of another investigation, in which it was required to synthesize 5-chloro-substituted derivatives of the type of (V).



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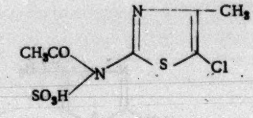


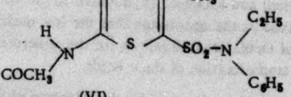
(V)

In order to obtain the starting material for the synthesis of these compounds, i.e., the chloro-substituted sulfochloride, we followed the method indicated in our preceding communication: action of chlorosulfonic acid on 2-acetamino-4-methyl-5-chlorothiazole. To our surprise, this compound did not enter into reaction with chlorosulfonic acid. The 5-bromo-derivative proved to be equally inert to chlorosulfonic acid. We, therefore, tried to prepare the required halogen derivative (V) by halogenating the sulfochloride of 2-acetamino-4-methylthiazole. However, the action of bromine in chloroform solution on the sulfochloride failed to give the anticipated bromo derivative and the sulfochloride was recovered unchanged. By contrast, in the same conditions 2-acetamino-4-methylthiazole, i.e., a compound without a substituent in the 5-position, is smoothly brominated with formation of the corresponding 5-bromo derivative.

All this led up to the idea that, contrary to former conclusions, in the chlorosulfonation of 2-acetamino-4-methylthiazole it is not the hydrogen of the acetamino group but the hydrogen in the 5-position in the ring which is substituted. Only thus can we account for the failure to realize the halogenation of the sulfochloride or the sulfochlorination of 5-halogen-substituted derivatives.

The following experiments provided further proof of the accuracy of this conclusion.

The action of ethylaniline on the sulfochloride of 2-acetamino-4-methylthiazole gave a disubstituted sulfamide. If the sulfochloride group is in the 5-position, then reaction with ethylaniline must give the amide of structure (VI), but if the sulfochloride group was located at the amino group, then a product of structure (VII) should have been formed.



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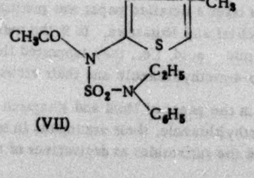

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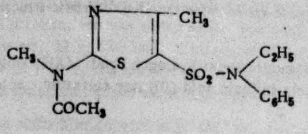
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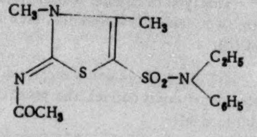
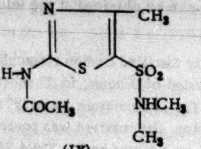
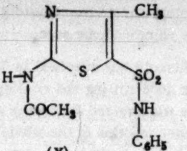

(VIIIa)

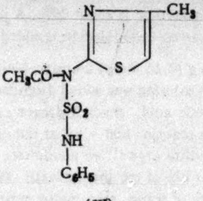
The substance with structure (VI) contains the acetamino group and should, therefore, like 2-acetamino-4-methylthiazole (IV), be soluble in caustic alkali and should be susceptible to methylation with dimethyl sulfate. But if the substance had structure (VII), then it should not dissolve in alkali and should not be methylated by dimethyl sulfate. Experiment showed that the disubstituted amide is readily soluble in caustic alkali and is smoothly methylated by dimethyl sulfate with formation in good yield of a product to which the structure of (VIII) or (VIIIa) can be ascribed. Consequently, we must assign structure (VI) to the starting substance.

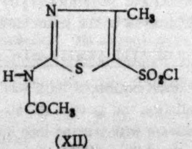
Structure (VI) for the disubstituted amide is also confirmed by the fact that the product reacts with CH_3MgI, and on analysis by the Chugaev-Tserevitinov method loses 1 mole methane per mole of substance; product (VIII) naturally cannot react with an organomagnesium compound.

These observations were further strengthened by the determination of the active hydrogen content by the Chugaev-Tserevitinov method in the starting substance—2-acetamino-4-methylthiazole (IV)—as well as in the dimethylsulfamide (IX) and the sulfanilide (X) prepared from the sulfochloride. One active hydrogen was detected in 2-acetamino-4-methylthiazole (IV), and the same in the dimethylsulfamide (IX), thereby confirming their structure. The anilide was found, in agreement with structure (X), to have two active hydrogens. If the anilide had possessed structure (XI), then it would have contained only one active hydrogen.


(IX)


(X)


(XI)


(XII)

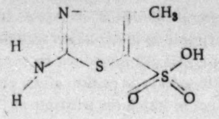
In the light of all the foregoing facts, we can confidently conclude that in the sulfamides of 2-acetamino-4-methylthiazole and correspondingly in the sulfamides of 2-acetaminothiazole, the sulfamide group is in the 5-position of the thiazole ring. It, therefore, follows that also in the starting sulfochloride of 2-acetamino-4-methylthiazole, the SO_2Cl group is in the same position, i.e., the sulfochloride is a derivative of the sulfonic acid (III) and has structure (XII).

At the start of the paper it was indicated that on hydrolysis the sulfochloride changes into the acid with m.p. 253° to which Ochiai and Nagasawa [1] and later Hurd and Kharasch [5] assigned the structure of the sulfamic acid (II). These conclusions were based mainly on the fact that the acid with m.p. 253° rearranges to the higher melting acid, which they assumed to be the sulfonic acid. In explanation of this phenomenon of rearrangement in the 2-aminothiazole series, an analogy was mechanically drawn with the known rearrangement of benzenesulfamic acid into sulfanilic acid.

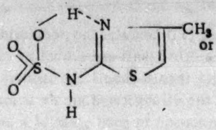
Since it has now been shown that the sulfochloride has structure (XII), it follows that the acid derived from it with m.p. 253° is the sulfonic acid (III); consequently, the acid into which compound (III) changes when heated with strong sulfuric acid must be regarded as the sulfamic acid (II).

This type of unusual rearrangement of a sulfonic acid into a sulfamic acid is here encountered for the first time. It is evidently associated, here in the 2-aminothiazole series, with the characteristic structure of the sulfamic acid (II).

For this acid we can postulate a structure with an intramolecular hydrogen bond[*] (XIII) which strengthens the molecule; if this is correct, the possibility of transition from sulfonic acid (III) into sulfamic acid (XIII) becomes understandable:

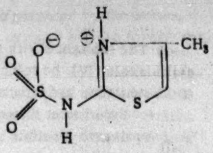


(III)



(XIII)

or



(XIIIa)

The conclusions drawn in this paper about the structure of the sulfochloride and the products derived from it have been confirmed by the infrared spectra of the compounds here described.

EXPERIMENTAL

(With participation of V. V. Kushkina)

Preparation of Low-Melting Sulfonic Acid (III)

According to Hurd and Kharasch [5] the low-melting acid with m.p. 256° (with decomposition) is obtained by adding chlorosulfonic acid to 2-amino-4-methylthiazole in carbon tetrachloride solution. The yield of recrystallized acid by this method is about 40%. A better yield and an immediately pure acid can be obtained if the solution of amine in carbon tetrachloride is added to the chlorosulfonic acid.

17.5 g (0.15 mole) 2-amino-4-methylthiazole was dissolved in 75 ml freshly distilled carbon tetrachloride. The amine solution was added dropwise, with good stirring and cooling over a period of 3 hours, to 22 ml (0.3 mole) chlorosulfonic acid. Much hydrogen chloride was evolved during the reaction. The temperature was −12° at the start of the reaction and + 14° at the end. After addition of the whole of the amine, the mixture was poured on to ice. The white crystalline precipitate was filtered, washed with water and dried on a water bath. Yield 23 g sulfonic acid (79% of the theoretical). M.p. 253-256° (with decomposition).[**] After recrystallization from ten times the quantity of water, rectangular prisms were obtained; m.p. unchanged.

The same acid was prepared by Ochiai and Nagasawa [1] by the action of strong sulfuric acid with cooling on 2-amino-4-methylthiazole, and also by hydrolysis of the sulfochloride (XII) [2].

Preparation of High-Boiling Acid (II) (Sulfamic Acid)

To 30 ml strong sulfuric acid in a round-bottomed flask was gradually added, with cooling, 20 g freshly distilled 2-amino-4-methylthiazole. The solution was heated at 150-165° on an oil bath for 5 hours. The mixture was then cooled to 40-50° and run in a fine stream with stirring into iced water. The brown precipitate was drained, washed with water and dried in the air. Yield 26 g (76%). The acid was recrystallized from 650 ml water with addition of active carbon. The colorless, large, polyhedral prisms did not melt when heated to 350°.

Formation of the Acid Chloride from the Low-Melting Acid

9.4 g (0.1 mole) low-melting sulfonic acid (m.p. 254-256°) was added in the cold to a solution of 0.4 g (0.1 mole) NaOH in 15 ml water. The solution was evaporated to dryness in a beaker on a water bath. The salt was recrystallized from a little water.

To 7.7 g sodium salt (about 0.03 mole) in a round-bottomed flask, fitted with an air condenser, was added 17 ml acetic anhydride, and the mixture heated at the boil for 2 hours. The contents of the flask were then cooled, and the precipitate was filtered, thoroughly washed with ether and dried on a water bath (yield 8.8 g). The acetyl derivative of the sulfonic acid was stirred with 15 g PCl_5 (about 0.06 mole), the mixture was thoroughly triturated and then transferred to a small round-bottomed flask, fitted with a reflux condenser, and heated for 2-2½ hours on a water bath. The mixture was gradually diluted during this process. After the conclusion of the reaction and cooling of the reaction mixture, ice was added to it. The curdy yellow product was filtered off, washed with cold water and dried in the air. M.p. 134-136°. Two recrystallizations from trichloroethylene gave 1.2 g colorless needles with m.p. 156-157°. A mixed sample with the sulfochloride prepared by the action of chlorosulfonic acid on 2-acetamino-4-methylthiazole melted without depression.

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[*] Another possibility is the polar, betaine structure (XIIIa). The problem of the unusual structure of the sulfamic acid may be finally clarified by determination of the dipole moments of the sulfonic acids.

[**] Without correction.

The same sulfochloride with m.p. 156° was obtained by the action of chlorosulfonic acid on the sodium salt of the acetyl derivative. The yield, however, was low (8.8 g salt gave 0.9 g sulfochloride).

Determination of Active Hydrogen in 2-Acetamino-4-methylthiazole

The investigated sulfamides are poorly soluble in anisole and amyl ether, but readily soluble in pyridine; all the active hydrogen determinations were, therefore, performed in pyridine solution.

The following method was found convenient for the preparation of substantially perfectly dry pyridine. After drying the pyridine by the usual method (distillation over KOH), it was transferred to a distilling flask and methylmagnesium iodide in anisole was added until bubbles of methane ceased to come off; then a small additional amount of methylmagnesium iodide was added and the pyridine distilled into a receiver provided with means for excluding atmospheric moisture. The pyridine so prepared did not cause methane evolution in a blank test with organomagnesium compound.

0.1385 g sub.: 23.2 ml CH_4 (24°, 740 mm). 0.2658 g sub.: 50.8 ml CH_4 (24°, 741 mm). Found active hydrogen (Chugaev-Tserevitinov method): 1.07, 1.19. $C_6H_8ON_2S$. Active hydrogen calculated: 1.00.

2-Acetamino-4-methyl-5-thiazolesulfone-N-ethylanilide (VI)

2.5 g (0.01 mole) 2-acetamino-4-methyl-5-thiazolylsulfonyl chloride was gradually run at room temperature with stirring into a solution of 1.2 g (0.01 mole) ethylaniline in 5 ml dry pyridine. The mixture, after standing for 24 hours, was poured into 100 ml cold water. The light-yellow product was filtered, well washed with water and dried in the air. Yield 3 g (91%): m.p. 187-189°. Recrystallization from aqueous alcohol (1:1) gave 2.6 g colorless prisms; m.p. 188-189°.

2.900 mg sub.: 0.328 ml N_2 (22°, 726 mm). 4.090 mg sub.: 0.465 ml N_2 (23°, 726 mm). 0.1053 g sub.: 7.2 ml CH_4 (20°, 735 mm). 0.1081 g sub.: 7.6 ml CH_4 (24°, 741 mm). Found %: N 12.52, 12.54; active hydrogen content (Chugaev-Tserevitinov) 0.93, 0.95. $C_{14}H_{17}O_3N_3S_2$. Calculated %: N 12.39; active hydrogen content 1.00.

Methylation of Compound (VI)

1.7 g (0.005 mole) substance (VI) was methylated in 1 N NaOH solution with dimethyl sulfate (2.5 ml). The product which separated on standing was filtered, washed with water, dried in the air and recrystallized from 35 ml dilute alcohol (1:1). Yield 1.3 g (74%); m.p. 128-129°. No change in m.p. after a second recrystallization. When the solution is cooled rapidly, the product crystallizes in rhombic form; on slow cooling it forms needles. The product does not react with CH_3MgI, i.e., it does not contain active hydrogen.

4.610 mg sub.: 0.495 ml N_2 (20°, 726 mm). 5.390 mg sub.: 0.557 ml N_2 (19°, 726 mm). Found %: N 11.95, 11.63. $C_{15}H_{19}O_3N_3S_2$. Calculated: N 11.89.

2-Acetamino-4-methyl-5-thiazolesulfone-dimethylamide (IX)

5.6 g (0.02 mole) sulfochloride (XII) was dissolved in 10 ml dry pyridine. Through the solution, externally cooled with ice, was passed a steady stream of dimethylamine prepared by decomposition of dimethylamine hydrochloride with alkali and drying over KOH. After saturation with dimethylamine, the solution was diluted with 100 ml water and then acidified with acetic acid to separate the amide. Yield 4.9 g (93%). M.p. 242-243°. Recrystallization from dilute alcohol (1:1) gave colorless leaflets with the same melting point.

Analysis for nitrogen by Pregl's method gave results 1% too low. Correct results were obtained in Kjeldahl analyses (semimicro).

0.0410 g sub.: 4.76 ml 0.1 N H_2SO_4. 0.0394 g sub.: 4.53 ml 0.1 N H_2SO_4. 0.0385 g sub.: 4.43 ml 0.1 N H_2SO_4. 0.1403 g sub.: 13.2 ml CH_4 (17°, 729 mm). 0.1819 g sub.: 16.8 ml CH_4 (17°, 732 mm) Found %: N 16.25, 16.09, 16.10; active hydrogen content (Chugaev-Tserevitinov) 0.99, 0.98. $C_8H_{13}O_3N_3S_2$. Calculated %: N 15.96; active hydrogen 1.00.

SUMMARY

1. It is shown that the action of chlorosulfonic acid on 2-acetamino-4-methylthiazole gives 2-acetamino-4-methylthiazole-5-sulfochloride (XII). Hydrolysis of the sulfochloride gives a sulfonic acid with m.p. 253-256°. The structure of a sulfamic acid attributed to this acid by Ochiai, Hurd and other authors is erroneous.

2. The observed transformation, on heating with strong sulfuric acid, of the acid with m.p. 253-256° into an acid with decomposition temperature above 340° must be regarded as an unusual case of transformation of a sulfonic acid (III) into a sulfamic acid (II) possessing the characteristic structure (XIII) or (XIIIa).

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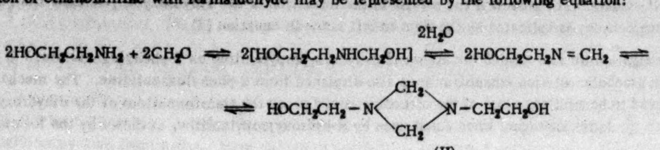
PREPARATION AND PROPERTIES OF 1,3-DIHYDROXYETHYLTETRAHYDRO-1,3-DIAZINE AND 2-PHENYLOXAZOLIDINE

K. D. Petrov, E. S. Lagucheva and V. I. Pukhova

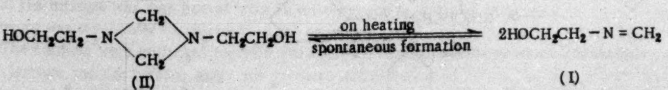
In a paper published in 1949, Paquin [1] states that ethanolamine reacts with formaldehyde to form 1,3,5-trihydroxyethylhexahydro-1,3,5-triazine. According to our own observations, however, this reaction proceeds with formation of 1,3-dihydroxyethyltetrahydro-1,3-diazine (II) (see [2]). In agreement with the experimental data the reaction of ethanolamine with formaldehyde may be represented by the following equation:



(II) (1)

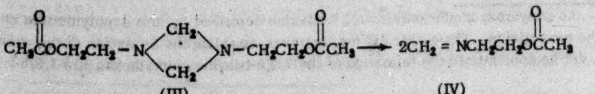
Experiments show that this reaction is best performed in benzene, the water being eliminated from the sphere of reaction with the solvent. This facilitates the left-to-right course of reaction (1) and the formation of the dihydroxyethyldiazine in a purer form.

The dihydroxyethyldiazine has the appearance of a viscous, colorless oil, n_D^{20} 1.5192. On heating followed by distillation, it changes into a readily mobile liquid with n_D^{20} 1.4740. On standing, however, this liquid again quickly changes into the dihydroxyethyldiazine. It is interesting to note that the process of transformation of the liquid into the dihydroxyethyldiazine sometimes proceeds so energetically that the temperature rises to 70-90°. Concerning the structure of the liquid, this could not be established by a direct method, due to its instability. It is extremely probable, however, that it is methyleneethanolamine (I) whose formation from the dihydroxyethyldiazine (II) proceeds according to equation (2)



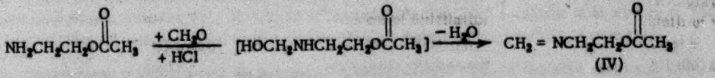
(II) (I) (2)

This is clear from the following fact. On acetylating the dihydroxydiethyldiazine with acetic anhydride and attempting to distil the product of acetylation in vacuum, we obtained in place of the expected diacetyl derivative of the dihydroxyethyldiazine (III) the acetate of methyleneethanolamine (IV). The formation in this case of the acetate of methyleneethanolamine can be explained as follows. Acetic anhydride first acts on the dihydroxydiethyldiazine to form the diacetate of the dihydroxyethyldiazine (III). In the course of the distillation, however, (III) depolymerizes with formation of the acetate of methyleneethanolamine (IV) as represented by equation (3)



(III) (IV) (3)

Formation of methyleneethanolamine acetate (IV) was confirmed by analysis for nitrogen and molecular weight determination. Apart from this, we prepared for comparison the same acetate by another route (4)



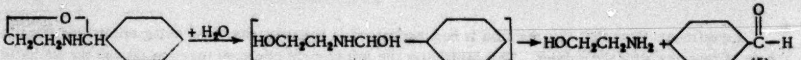
$$NH_2CH_2CH_2OCCH_3 \xrightarrow[+HCl]{+CH_2O} [HOCH_2NHCH_2CH_2OCCH_3] \xrightarrow{-H_2O} \underset{(IV)}{CH_2=NCH_2CH_2OCCH_3} \quad (4)$$

Methyleneethanolamine acetate prepared by route (4) corresponded in boiling point, specific gravity and refractive index to the product (IV) obtained in the process of distillation (heating) of the diacetate of the dihydroxyethyldiazine (III). It was thus proved that the product of depolymerization of the diacetate of the dihydroxyethyldiazine is undoubtedly methyleneethanolamine acetate. At the same time it was confirmed that the above scheme (2) for transition of the dihydroxyethyldiazine itself into methyleneethanolamine corresponds to the facts.•

Subsequently, we studied the reaction of the dihydroxyethyldiazine with β-hydroxypropylaniline, when it was observed that, when performing the reaction in non-anhydrous alcohol, ethanolamine and 5-methyl-3-phenyloxazolidine were formed. It goes without saying that the formation of these compounds is bound up with the conversion of the dihydroxyethyldiazine into ethanolamine and formaldehyde; we actually isolated the ethanolamine in the free state. The formaldehyde formed in these conditions reacts in known manner [3] with β-hydroxypropylaniline to form 5-methyl-3-phenyloxazolidine.

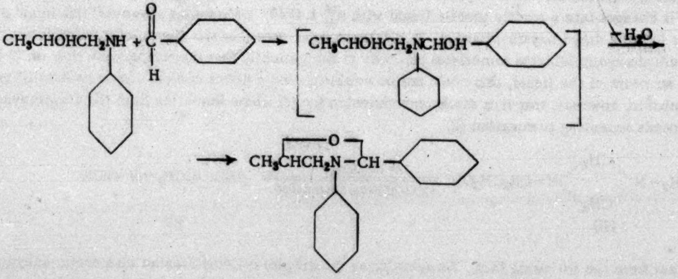
Concerning the mechanism of transformation of the dihydroxyethyldiazine into ethanolamine and formaldehyde, this is self-evident. The process is the reverse of the formation of the dihydroxyethyldiazine from ethanolamine and formaldehyde, as indicated by the right-to-left arrow in equation (1).

In this investigation we also studied the action of β-hydroxypropylaniline on 2-phenyloxazolidine. It was established that in alcoholic solution ethanolamine is also displaced from 2-phenyloxazolidine. The mechanism of the process proved to be similar to that of the preceding one, i.e., to the transformations of the dihydroxyethyldiazine which the latter undergoes when acted upon by β-hydroxypropylaniline, as shown by the following schemes (5, 6)



(5)

The benzaldehyde formed then reacts with β-hydroxypropylaniline to give 5-methyl-2,3-diphenyloxazolidine (V)



(6)

(V)

This observation is of interest since it illustrates some general properties of dihydroxyethyldiazine with oxazolidine derivatives: hydrolysis, formation of the same type of intermediate compounds (methylolethanolamines) and cleavage of the latter into aminoalcohols and aldehydes.

•Paquin considers that the 1,3,5-trihydroxyethylhexahydro-1,3,5-triazine described by him depolymerizes on heating with formation of the oxazolidine. The author did not, however, establish the formation of the oxazolidine, nor, strictly speaking, did he demonstrate the formation of the 1,3,5-trihydroxyethylhexahydro-1,3,5-triazine itself.

EXPERIMENTAL*

1. Preparation of 1,3-Dihydroxyethyltetrahydro-1,3-diazine (II)

Into a three-necked flask, fitted with stirrer, reflux condenser and water trap, were charged 122 g (2 moles) ethanolamine and 140 ml benzene. From a dropping funnel was gradually run in, with stirring, 163 g (36.70%) formaldehyde (approximately 2 moles CH_2O). At first the reaction proceeded spontaneously with evolution of heat; later the reaction mixture was heated on a bath to the boil. Water was removed from the sphere of reaction with the benzene vapor and collected in the trap. The process was continued until water ceased to come off. At the conclusion of the process, the reaction mass was fractionated in vacuum. Benzene and other volatiles (traces) were taken off in a low vacuum. An intermediate fraction came over at 60-92° and 6 mm in the form of a readily mobile colorless liquid, 22 g. On standing, this liquid changed into a viscous oil whose refractive index (n^{20}_D 1.51[illegible]) was close to that of the dihydroxyethyldiazine. The main fraction came over at 92-97° and 6-5 mm and was a readily mobile, colorless liquid — methyleneethanolamine (I). Yield 88 g (60.28%). It was redistilled for further purification to give a narrower cut with boiling range 94-97° at 6 mm, 48 g; n^{20}_D 1.4740. After brief standing this liquid changed (with heat development) into a viscous, colorless oil whose nitrogen content and molecular weight corresponded to 1,3-dihydroxyethyltetrahydro-1,3-diazine (II); numerous observations show that the change of methyleneethanolamine into the dihydroxyethyldiazine is substantially completed after 6-10 hours. In the air the dihydroxyethyldiazine absorbs an appreciable amount of carbon dioxide.

d^{20}_{20} 1.1787; n^{20}_D 1.5192; MR_D 38.30; Calc. 38.63.

1.1233 g substance: 151.32 ml 0.1 N H_2SO_4. 1.3158 g substance: 176.66 ml 0.1 N H_2SO_4. 0.3200 g substance: 34.98 g water: Δt 0.115°. 0.3407 g substance: 35.14 g water: Δt 0.12°. Found %: N 18.85, 18.79; M 147.14, 149.47. $C_6H_{14}O_2N_2$. Calculated %: N 19.13; M 146.

We also performed the reaction of ethanolamine with formaldehyde in the conditions described by Paquin [1], i.e., without removing the water from the sphere of reaction. The dihydroxyethyldiazine was then obtained in an insufficiently pure form and we were unable to purify it by repeated fractionations. The dihydroxyethyldiazine obtained by this method had the following constants:

d^{20}_{20} 1.1848; n^{20}_D 1.5186.

0.4259 g substance: 0.7938 g CO_2; 0.3805 g H_2O. 1.1695 g substance: 146.60 ml 0.1 N H_2SO_4. 1.5564 g substance: 194.60 ml 0.1 N H_2SO_4. 0.2250 g substance: 32.32 g water: Δt 0.09°. 0.2409 g substance: 37.17 g water: Δt 0.085°. Found %: C 50.83; H 9.99; N 17.54, 17.49; M 143, 141. $C_6H_{14}O_2N_2$. Calculated %: C 49.39; H 9.59; N 19.13; M 146.

2. Acetylation of 1,3-Dihydroxyethyltetrahydro-1,3-diazine

To 219 g (1.5 moles) 1,3-dihydroxyethyltetrahydro-1,3-diazine was gradually added from a dropping funnel 459 g (4.5 moles) acetic anhydride. After the whole amount had been added, the reaction mixture was heated for 8 hours at 95-100°. At the conclusion of the reaction, the excess anhydride was distilled off on an oil bath under vacuum; the mixture was then heated with 85 ml water and neutralized with saturated sodium carbonate solution. The product was repeatedly extracted from the aqueous solution with butanol and ether in the ratio of 1:1 by volume. The extracts were collected together and distilled. The solvent came over first; the ether was taken off at normal pressure and the butanol under low vacuum. Fractionation of the residue gave a main fraction at 107-109° and 7 mm weighing 115 g. This product was a readily mobile, colorless liquid. In nitrogen content and molecular weight it corresponded to the acetate of methyleneethanolamine (IV); b.p. 224-225° at 758 mm.

d^{20}_{20} 1.1474; n^{20}_D 1.4758; MR_D 28.30; Calc. 28.64 (without allowance for the double bond of $CH_2 = N$, whose value is not given in the literature). 0.3710 g sub.: 31.16 ml 0.1 N H_2SO_4. 1.0173 g sub.: 82.97 ml 0.1 N H_2SO_4. 0.9325 g sub.: 36.98 g water: Δt 0.405°. 1.5793 g sub.: 36.98 g water: Δt 0.71°. Found %: N 11.75, 11.42; M 115, 111.5. $C_5H_9O_2N$. Calculated %: N 12.17; M 115.

3. Preparation of Acetate of Methyleneethanolamine (IV) from β-Acetoxyethylamine and Paraformaldehyde

Into a flask, fitted with stirrer, reflux condenser and trap, were charged 51.5 g (0.5 mole) β-acetoxyethylamine, prepared by the method of Crane and Rydon [4], 16.5 g paraformaldehyde (0.55 mole CH_2O), 100 ml benzene and 5 ml hydrochloric acid (sp. gr. 1.19). The reaction was performed with heating and continuous stirring. The water formed during the reaction was entrained by the benzene and collected in the trap. The process was continued until water ceased to come off (10 ml was collected in all). At the end of the process, the product was neutralized with sodium carbonate solution, extracted with butanol and fractionated in vacuum. The methylene-ethanolamine acetate fraction was collected at 100-105° and 7-6 mm in amount of 30 g. For further purification it was redistilled to give a product with b.p. 103-104° at 6 mm, 14 g. Readily mobile liquid with b.p. 224-226° at 761 mm.

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*The molecular weights given in this paper were determined by A. L. Cherborovskaya, to whom we express our thanks.

d_{20}^{20} 1.1485; n_D^{20} 1.4762; MR_D 28.29; Calc. 28.64.

0.8001 g substance: 68.95 ml 0.1 N H_2SO_4, 0.7368 g substance: 62.80 ml 0.1 N H_2SO_4, 0.8606 g substance: 34.88 g water: Δt 0.42°. Found %: N 12.06, 11.94; M 108.67. $C_5H_9O_2N$. Calculated %: N 12.17; M 115.

4. Interaction of 1,3-Dihydroxyethyltetrahydro-1,3-diazine with β-Hydroxypropylaniline

In a flask with a ground-glass stopper were placed 72.8 g (0.498 mole) 1,3-dihydroxyethyltetrahydro-1,3-diazine, 120.8 g (0.8 mole) β-hydroxypropylaniline with b.p. 132-133° at 3 mm (n_D^{20} 1.5620) and 50 ml ethyl alcohol (not anhydrous). The reaction was conducted at room temperature for 8 hours. From time to time the mixture was shaken. The alcohol was distilled off on the boiling water bath when the reaction was concluded. The residue was distilled in vacuum through the column described by Kazansky and co-workers, fitted with a Whitmore-Lukes condenser and Fenske packing. The following fractions were collected:

1 60-82° at 8 mm – 9 g, n_D^{19} 1.4558;
2 82-85° at 8-10 mm – 23 g, n_D^{19} 1.4561;
3 85-130° at 10-11 mm – 7 g, n_D^{20} 1.5559;
4 130-132° at 10-11 mm – 21 g, n_D^{20} 1.5600;
5 132-134° at 10- 9 mm – 10 g, n_D^{20} 1.5600;
6 134-146° at 9-11 mm – 20 g, n_D^{20} 1.5605;
7 146-158° at 11-10 mm – 25 g, n_D^{20} 1.5625.

Of these fractions, the 2nd, 4th, and 5th were examined more closely. The second fraction was distilled at 762 mm to give 8 g substance with b.p. 170-173°. In boiling point and refractive index (n_D^{20} 1.4560) it corresponded to ethanolamine, the literature values for which [6] are b.p. 171° and n_D^{20} 1.4539. The product collected at 130-132° and 10-11 mm (4th fraction) solidified on standing to a white crystalline mass, readily soluble in alcohol. After two recrystallizations from alcohol, it melted at 37.5-38.5°. In melting point it was identical with 5-methyl-3-phenyloxazolidine (m.p. 37-38°) as described by Kon and Roberts [3]. A mixed sample with the 5-methyl-3-phenyloxazolidine prepared by the method of Kon and Roberts melted at 37.5-38.5°. The analytical data also corresponded to 5-methyl-3-phenyloxazolidine.

0.1485 g substance: 0.3993 g CO_2; 0.1131 g H_2O. Found %: C 73.34; H 8.50. $C_{10}H_{13}ON$. Calculated %: C 73.60; H 7.97.

The fifth fraction also solidified on standing to a white crystalline mass and was 5-methyl-3-phenyloxazolidine, melting after two recrystallizations from alcohol at 37.5-38.5°.

5. Interaction of 2-Phenyloxazolidine with β-Hydroxypropylaniline

37.25 g (0.25 mole) 2-phenyloxazolidine, prepared by the method of Knorr and Matthes [7], (b.p. 132-134° at 9-7 mm, n_D^{19} 1.5700), was stirred with 37.72 g (0.25 mole) β-hydroxypropylaniline and 50 ml alcohol (not anhydrous). The mixture was mechanically stirred for 8 hours at room temperature; the alcohol was then driven off on a boiling water bath and the residue fractionated in vacuum, the following being collected: 1st fraction, 35-141° at 30-9 mm, 30 g; 2nd fraction, 141-180° at 9-8 mm, 26 g; 3rd fraction, 180-193° at 8 mm, 16 g.

Of these the 1st and 3rd were examined; the 1st fraction was distilled at atmospheric pressure to give 2 g substance with b.p. 169-172° (n_D^{20} 1.4500), identified as ethanolamine [7]. The 3rd fraction solidified on standing to a white crystalline mass. The crystals were washed with alcohol. Yield 9 g. The product was subsequently washed with sodium carbonate solution and recrystallized from alcohol; it then melted at 87.2-88.5°. Its melting point was identical with that of 5-methyl-2,3-diphenyloxazolidine (m.p. 88.5-89.5°) and a mixture did not give a depression (the mixture melted at 87.2-88.5°). The analytical data also corresponded to 5-methyl-2,3-diphenyloxazolidine (V).

0.1440 g substance: 0.4242 g CO_2; 0.1014 g H_2O. 0.6958 g substance: 26.98 ml 0.1 N H_2SO_4. Found %: C 80.12; H 7.85; N 5.43. $C_{16}H_{17}ON$. Calculated %: C 80.33; H 7.12; N 5.85.

SUMMARY

1. The preparation of 1,3-dihydroxyethyltetrahydro-1,3-diazine and of the product of its acetylation is described.

2. It was established that the product of acetylation of 1,3-dihydroxyethyltetrahydro-1,3-diazine polymerizes when heated in vacuum and forms methylene-β-acetoxyethylamine.

3. It is shown that 1,3-dihydroxyethyltetrahydro-1,3-diazine reacts with β-hydroxypropylaniline to form ethanolamine and 5-methyl-3-phenyloxazolidine. A mechanism of this reaction is given.

4. The reaction of displacement of ethanolamine from 2-phenyloxazolidine by aromatic aminoalcohols is described. This phenomenon of hydraminolysis is here described for the first time.

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Institute of Research on Plastic Materials

SYNTHESIS OF DERIVATIVES OF 1-HYDROXYPHENAZINE

V. HALOGEN DERIVATIVES OF 1-METHOXYPHENAZINE

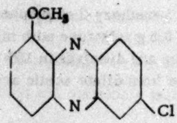
S. B. Serebryany and N. A. Ilyushina

In the first communication the synthesis of monochlorophenazines and of some dichlorophenazines was described [1].

In the present paper we consider the preparation of chloro derivatives of 1-methoxyphenazine. We prepared these compounds with the aim of further transforming them into chloro derivatives of N-alkylphenazinone-1.

Chloro derivatives of 1-methoxyphenazine were synthesized by alkaline condensation of o-nitroanisole with m- and p-chloroanilines. From the mixture of phenazine bases obtained by condensation of o-nitroanisole with p-chloroaniline was isolated 1-methoxy-7-chlorophenazine with m.p. 209-210°. This preparation was recently obtained by Vivian [2] by a complicated route from a derivative of 2-nitrodiphenylamine.

On condensation of o-nitroanisole with m-chloroaniline we should expect two chloro derivatives of 1-methoxyphenazine.



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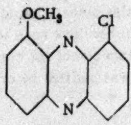

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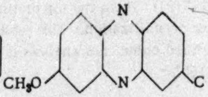

(III)

From the mixture of phenazine bases formed in this condensation, we actually isolated two chloro derivatives of 1-methoxyphenazine: light-yellow needles with m.p. 165-166° (I) and orange-yellow needles with m.p. 184-185° (II).

The position of the chlorine atoms in these preparations was established in the following manner: m-nitroanisole was brought into condensation with p-chloroaniline; two phenazine bases were formed: light-yellow needles with m.p. 165-168° and light-yellow needles with m.p. 150-151° (III). Both substances with m.p. 165-166° did not give a depression in a mixed test. Consequently, they are both identical with 1-methoxy-6-chlorophenazine (I). Hence, it follows that the preparation with m.p. 184-185° (II) is 1-methoxy-8-chlorophenazine, while the preparation with m.p. 150-151° (III) is 3-methoxy-6-chlorophenazine. The last substance was obtained by Vivian, m.p. 151-152° [2].

Employment of the chromatographic technique for resolution of the products of condensation enabled us to detect some secondary products of alkaline condensation in these reactions. Condensation of o-nitroanisole with chloro derivatives of aniline gives, apart from chloro derivatives of 1-methoxyphenazine, derivatives of phenazine not containing methoxyl groups.

Thus, on condensation of o-nitroanisole with p-chloroaniline, 2-chlorophenazine is formed in addition to 1-methoxy-7-chlorophenazine. From the mixture of phenazine bases obtained by condensation of o-nitroanisole with m-chloroaniline, 1- and 2-chlorophenazines were isolated in addition to the 6- and 8-chloro derivatives of 1-methoxyphenazine. We also detected dimethoxyphenazines in the mixture of condensation products; from the products of condensation of o-nitroanisole with p-chloroaniline was isolated 1,7-dimethoxyphenazine, while the products of reaction of o-nitroanisole with m-chloroaniline included 1,8-dimethoxyphenazine.

EXPERIMENTAL

Alkaline condensation was conducted in a three-necked reactor which was equipped with a mercury-sealed stirrer and a reflux condenser. The latter was connected to the reactor via a Dean and Stark trap. Into the reactor were charged the nitro compound and the amine (in 1:1 molar ratio); potassium hydroxide powder was dropped in and toluene was added. The reaction mixture was boiled for 7 hours. At the end of the reaction the contents were cooled and poured into 1 liter water. The toluene layer was diluted with three times the volume of solvent and separated from the alkali solution. The solvent and the unreacted starting materials were distilled off with steam. The residue after the distillation was dissolved in dichloroethane and worked up with 20% hydrochloric acid (3-4 times with 100-150 ml each time). The combined acid extracts were filtered and treated with aqueous ammonia. The separated mixture of phenazine bases was dissolved in benzene and chromatographed on alumina. The chromatogram was developed with benzene. The phenazine derivatives distributed over the various zones were separated mechanically. Each zone was eluted with a mixture of alcohol and benzene. The solvents were drawn off to leave a small volume and the phenazine base was separated by treatment with 20% hydrochloric acid followed by precipitation with aqueous ammonia. In some cases for complete resolution of the mixture, the chromatogramming was repeated several times.

1-Methoxy-7-chlorophenazine. A mixture of 15.3 g o-nitroanisole, 12.8 g p-chloroaniline, 28 g KOH and 150 ml toluene was heated 7 hours. In all, 2.11 g of impure mixture of phenazine bases was obtained. Three zones were observed when the chromatogram was developed: lower one, light-yellow; middle one, yellow; top one, yellow-brown.

From the bottom zone was isolated 0.8 brownish-yellow needles with m.p. 135-138°. Crystallization from alcohol gave light-yellow needles with m.p. 139-140°. The preparation dissolves in 15% hydrochloric acid with a yellow color. A mixed test with 2-chlorophenazine did not give a depression. This substance is therefore 2-chlorophenazine. Yield 3.7% of the theoretical. From the middle yellow zone was isolated 0.45 g yellow needles with m.p. 198-202°. The preparation dissolves in 15% hydrochloric acid with a red color and contains chlorine. It was purified by recrystallization from ligroine. Brownish prisms with m.p. 209-210°.

Found %: N 11.32, 11.50. $C_{13}H_9ON_2Cl$. Calculated %: N 11.45.

The analysis and chemical properties of this preparation identify it as 1-methoxy-7-chlorophenazine (Vivian reports m.p. 209-211° [2]). From the top brownish-yellow zone was isolated 0.5 g substance with m.p. 150°. No change in m.p. after crystallization. This substance does not contain chlorine and dissolves in 15% hydrochloric acid with a brownish-red color. For analysis it was purified by crystallization from dilute acetic acid. Yellow needles with m.p. 150°.

Found %: N 11.63, 11.68. $C_{14}H_{12}O_2N_2$. Calculated %: N 11.66.

The preparation melts at the same temperature as 1,7-dimethoxyphenazine [3] and does not give a depression in admixture with it. Yield 2.1% of the theoretical. Total yield of phenazine bases 7.6% of theoretical.

1-Methoxy-6-chloro- and 1-methoxy-8-chlorophenazines. A mixture of 15.3 g o-nitroanisole, 12.8 g m-chloroaniline and 25 g KOH in 150 ml toluene was boiled for 7 hours. 3.51 g of a mixture of phenazine bases was isolated. Chromatographic resolution of the benzene solution gave three zones: lower one, light-yellow; middle one, yellow, and top one, brown-yellow. A mixture of compounds was found to be adsorbed in each zone. The eluates of the bottom and middle zones, after removal of the alcohol, were therefore again chromatogrammed on alumina. The bottom zone then yielded two substances:

1) 0.23 g greenish-yellow needles with m.p. 115-117°; this compound was located in the lower part of the chromatogram. It contains halogen and dissolves in 15% hydrochloric acid with a yellow color. Crystallization from alcohol gave light-yellow needles with m.p. 20-22°. A mixed test with 1-chlorophenazine did not give a depression.

2) 0.8 g brownish-yellow needles with m.p. 135-138°; the preparation contains halogen and dissolves in 15% hydrochloric acid with a yellow color. Crystallizes from alcohol as light-yellow needles with m.p. 139-140°. A mixed test with 2-chlorophenazine did not give a depression. Yield of chlorophenazines, 4.9% of the theoretical. Chromatogramming of the eluate of the middle zone from the original chromatographic treatment gives the following picture: in visible light two zones are not observed, but in ultraviolet light two zones can be clearly distinguished – a lower yellow one and an upper greenish-yellow one.

The usual treatment of the lower zone gave 1-methoxy-8-chlorophenazine in the form of small orange-yellow needles with m.p. 184-185°. The preparation was purified for analysis by crystallization from ligroine.

Small orange-yellow needles with m.p. 184-185°.

Found %: N 11.20, 11.16; Cl 14.40, 14.49. $C_{13}H_9ON_2Cl$. Calculated %: N 11.45; Cl 14.49.

From the upper greenish-yellow zone was isolated a substance with m.p. 140-152°. This was evidently a mixture of two phenazine bases. Repeated chromatogramming of the benzene solution of this mixture on alumina led to isolation of a compound with m.p. 160-161° and a further quantity of 1-methoxy-8-chlorophenazine with m.p. 184-185°. The 1-methoxy-6-chlorophenazine with m.p. 160-161° was recrystallized from aqueous alcohol prior to analysis. Yellow needles, m.p. 165-166°.

Found %: N 11.30; Cl 14.31. $C_{13}H_9ON_2Cl$. Calculated %: N 11.45; Cl 14.49.

Both preparations dissolve in 15% hydrochloric acid with a red color. A total of 1.65 g 1-methoxy-8-chlorophenazine with m.p. 184-185° was obtained and 0.57 g 1-methoxy-6-chlorophenazine with m.p. 160-161°. The yield of these bases was 9.1% of the theoretical. From the eluate of the upper brownish-yellow zone of the original chromatogram, after concentration of the solvent to a small volume, crystallized brownish-yellow needles with m.p. 254-255°. This substance does not contain halogen and dissolves in 15% hydrochloric acid with a dark-red color. For purification it was crystallized from ligroine. Long, filiform, bright-yellow needles with m.p. 259-260°. A mixed test with 1,8-dimethoxyphenazine [4] did not give a depression. From the mother liquor was isolated a mixture of phenazine bases. Chromatographic resolution of this mixture yielded a further quantity of 1,8-dimethoxyphenazine and a mixture of methoxychlorophenazines. A total of 0.15 g 1,8-dimethoxyphenazine was obtained. The total yield of phenazine bases obtained by condensation of o-nitroanisole with m-chloroaniline is 14.1% of the theoretical.

1-Methoxy-6-chloro- and 3-methoxy-6-chlorophenazines. A mixture of 7.7 g m-nitroanisole, 6.4 g p-chloroaniline, 13 g KOH and 75 ml toluene was boiled for 7 hours. Chromatographic resolution on alumina of the mixture of phenazine bases from benzene solution gave two zones: lower one, light-yellow, and upper one, yellow. From the lower one was isolated brownish-yellow needles with m.p. 150-151°. The preparation dissolves in 15% hydrochloric acid with a yellow color. For analysis the preparation was purified by crystallization from aqueous alcohol. Small, light-yellow needles, m.p. 150-151°.

Found %: N 11.13. $C_{13}H_9ON_2Cl$. Calculated %: N 11.45.

From the upper zone was isolated a preparation with m.p. 160-162°, soluble in 15% hydrochloric acid with a red color. After crystallization from aqueous alcohol it melted at 165-166°. The yield of phenazine bases in this condensation is relatively low and amounts to 1.2% of the theoretical.

The authors are extremely grateful to Prof. A. I. Kiprianov for valuable advice and guidance during the research.

SUMMARY

1. 1-Methoxy-7-chlorophenazine is obtained by alkaline condensation of o-nitroanisole with p-chloroaniline.

2. Condensation of o-nitroanisole with m-chloroaniline and of m-nitroanisole with p-chloroaniline gives a mixture of chloro derivatives of 1-methoxyphenazine: in the first case a mixture of 1-methoxy-6-chloro- and 1-methoxy-8-chlorophenazines; in the second a mixture of 1-methoxy-6-chloro- and 3-methoxy-6-chlorophenazines. These mixtures were resolved by chromatogramming of their benzene solutions on alumina.

3. Condensation of o-nitroanisole with chloroanilines gives, apart from derivatives of 1-methoxyphenazine, derivatives of phenazine and dimethoxyphenazines.

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The authors are extremely grateful to Prof. A. I. Kiprianov for valuable advice and criticism during the research.

SUMMARY

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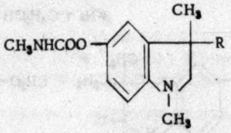
SYNTHETIC INVESTIGATIONS OF INDOLE DERIVATIVES

II. SYNTHESIS OF THE METHYLURETHANES OF 1,3,3-TRIMETHYL-5-HYDROXYINDOLINE AND 1,3-DIMETHYL-3-ETHYL-5-HYDROXYINDOLINE

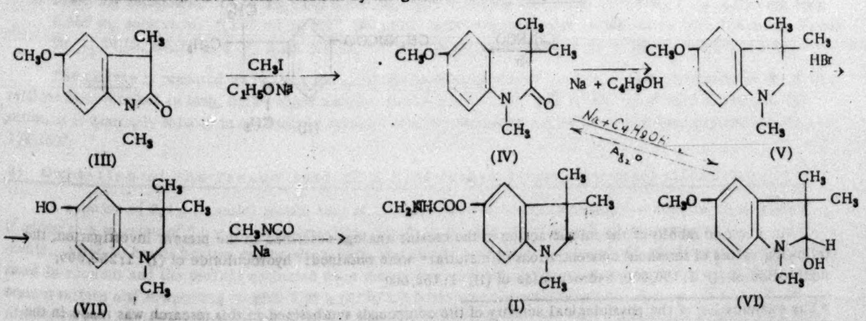
M. N. Kolosov and N. A. Preobrazhensky

In the preceding communication [1] we described the synthesis and properties of methylurethanes (methylcarbamic esters) of 1-methyl-5-hydroxyindoline and of 1,3-dimethyl-5-hydroxyindoline (dihydrophysostigmol). The present research was undertaken with the objective of obtaining the methylurethanes of 3,3-dialkyl derivatives of 1-methyl-5-hydroxyindoline, namely, of 1,3,3-trimethyl-5-hydroxyindoline (I) and 1,3-dimethyl-3-ethyl-5-hydroxyindoline (II). These analogs of eserine are of interest in connection with the still closer resemblance of their hydrocarbon skeleton to that arrangement of carbon atoms which occurs in the molecule of the natural alkaloid, eserine. Moreover, the whole series of urethanes described in the present and in the previous communications are interesting from the standpoint of study of the dependence of the physiological action of compounds of this type on the number and size of the alkyl groups in the 3-position of the indoline ring.

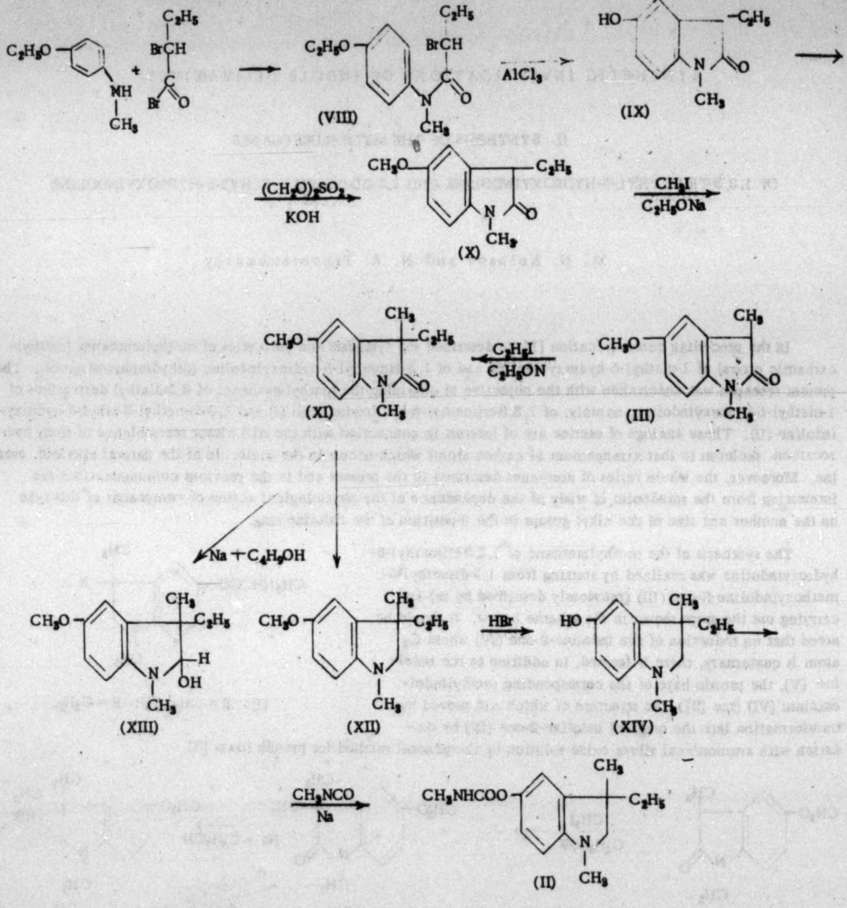


(I): R = CH$_3$; (II): R = C$_2$H$_5$.

The synthesis of the methylurethane of 1,3,3-trimethyl-5-hydroxyindoline was realized by starting from 1,3-dimethyl-5-methoxyindoline-2-one (III) (previously described by us) and carrying out the steps shown in the scheme below. It should be noted that on reduction of the indoline-2-one (IV) whose C$_3$ atom is quaternary, there is formed, in addition to the indoline (V), the pseudo base of the corresponding methylindoleninium (VI) (see [2]), the structure of which was proved by transformation into the original indoline-2-one (IV) by oxidation with ammoniacal silver oxide solution by the general method for pseudo bases [3].



The synthesis of the methylurethane of 1,3-dimethyl-3-ethyl-5-hydroxyindoline (II) was performed with starting materials in the form of both 1,3-dimethyl-5-methoxyindoline-2-one (III) and 1-methyl-3-ethyl-5-methoxyindoline-2-one (X); the latter is readily obtained by the known reaction of arylides of α-haloacids from the N-methylphentidide of α-bromobutyric acid (VIII).



In a test on rabbits of the miotic action of the eserine analogs described in the present investigation, the following values of threshold concentrations of material* were obtained: hydrochloride of (I) 1:250,000; methiodide of (I) 1:100,000; hydrochloride of (II) 1:150,000.

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* The examination of the physiological activity of the compounds synthesized in this research was made in the S. Ordzhonikidze Research Institute of Pharmaceutical Chemistry by I. M. Sharapov under the direction of Prof. M. D. Mashkovsky to whom the authors express their deep gratitude.

EXPERIMENTAL

1) 1,3,3-Trimethyl-5-methoxyindoline-2-one

To a solution of 20.0 g (1.00 mole) of 1,3-dimethyl-5-methoxyindoline-2-one [1] in 60 ml absolute alcohol and 44.5 g (3 moles) methyl iodide, stirred at 50°, is added in the course of 2 1/2 hours a solution of 4.8 g (2 g-atoms) sodium in 150 ml absolute alcohol. Stirring is continued at the same temperature for another 2 hours. The alcohol is then taken off in vacuum and the residue is dissolved in 50 ml water and 100 ml ether. The ethereal extract is washed with sodium bisulfite solution and water and dried with sodium sulfate before the ether is distilled off. Distillation of the residue gives 18.7 g (87%) of 1,3,3-trimethyl-5-methoxyindoline-2-one with b.p. 152-153° at 6.5 mm. After crystallization from ether the substance has m.p. 58.5-59.0°; its mixture with 1,3-dimethyl-5-methoxyindoline-2-one has m.p. 45-47°.

3.000 mg substance: 7.730 mg CO_2; 2.005 mg H_2O. 2.990 mg substance: 7.700 mg CO_2; 2.020 mg H_2O. 4.535 mg substance: 0.284 ml N_2 (24°, 746 mm). 5.285 mg substance: 0.314 ml N_2 (24°, 744 mm). Found %: C 70.27, 70.23; H 7.48, 7.56; N 6.99, 6.69. $C_{12}H_{15}O_2N$. Calculated %: C 70.21; H 7.37; N 6.82.

2) 1,3,3-Trimethyl-5-methoxyindoline (V) and the Pseudo Base of 3,3-Dimethyl-5-methoxy-methylindoleninium (VI)

To a boiling solution of 13.5 g (1 mole) 1,3,3-trimethyl-5-methoxyindoline-2-one in 600 ml absolute butanol is added 60 g (39.6 g-atoms) sodium. The reaction mixture is heated until a precipitate begins to come down, another 300 ml absolute butanol is run in and heating is continued until the sodium has completely dissolved. The partly cooled solution is washed several times with water and the alcohol is distilled off in vacuum. The residue is dissolved in 30 ml water and 50 ml ether, the ethereal solution is washed with water and the bases are extracted with 10% hydrochloric acid (about 30 ml). The acid solution is made alkaline, the supernatant oil is extracted with ether. The dried (with magnesium sulfate) extract is evaporated and the residue is distilled. Three fractionations give 5.01 g (40%) 1,3,3-trimethyl-5-methoxyindoline with b.p. 118-120° at 6 mm and 4.55 g (33%) pseudo base of 3,3-dimethyl-5-methoxy-methylindoleninium with b.p. 154-157° at 6 mm.

The hydrochloride of 1,3,3-trimethyl-5-methoxyindoline is obtained in 85% yield by passing a stream of dry hydrogen chloride into a concentrated alcoholic solution of the base. After recrystallization from alcohol, it forms colorless needles with m.p. 203.0-203.5°.

2.935 mg substance: 6.810 mg CO_2; 1.985 mg H_2O. 3.010 mg substance: 7.000 mg CO_2; 2.100 mg H_2O. 4.840 mg substance: 0.274 ml N_2 (25°, 748 mm). 4.770 mg substance: 0.264 ml N_2 (21°, 753 mm). Found %: C 63.28, 63.43; H 7.57, 7.81; N 6.39, 6.37. $C_{12}H_{18}ONCl$. Calculated %: C 63.27; H 7.97; N 6.15.

The picrate of 1,3,3-trimethyl-5-methoxyindoline crystallizes from alcohol in yellow crystals with m.p. 151.5-152°.

The pseudo base of 3,3-dimethyl-5-methoxy-methylindoleninium is a difficultly mobile yellow oil, rapidly darkening on standing. The substance with b.p. 155° at 6 mm was taken for analysis.

2.985 mg substance: 7.610 mg CO_2; 2.230 mg H_2O. 2.980 mg substance: 7.645 mg CO_2; 2.205 mg H_2O. 4.250 mg substance: 0.255 ml N_2 (22°, 736 mm). 4.295 mg substance: 0.255 ml N_2 (20°, 738 mm). Found %: C 69.53, 69.97; H 8.36, 8.28; N 6.72, 6.72. $C_{12}H_{17}O_2N$. Calculated %: C 69.52; H 8.27; N 6.76.

The picrate is prepared by heating the alcoholic solution of the pseudo base with excess picric acid. It crystallizes from alcohol in long, dark-yellow needles with m.p. 155-156°. Like all the quaternary picrates in this series, it is sparingly soluble in alcohol; its mixture with the picrate of 1,3,3-trimethyl-5-methoxyindoline has m.p. 138-140°.

3) Oxidation of the Pseudo Base of 3,3-Dimethyl-5-methoxy-methylindoleninium

A solution of 2.4 g (1 mole) pseudo base of 3,3-dimethyl-5-methoxymethylindoleninium in 10 ml alcohol is added to a solution of 7.0 g (3.55 moles) silver nitrate in 25 ml alcohol and 15 ml concentrated aqueous ammonia. After 10 hours' heating on the water bath, the precipitated silver is filtered off, the filtrate is evaporated in vacuum and the product extracted from the residue with ether. The ethereal extract is dried with magnesium sulfate and evaporated to give 1.92 g (81%) 1,3,3-trimethyl-5-methoxyindoline-2-one with m.p. 54-57°. After recrystallization from ether the substance has m.p. 58-59° and does not give a depression in admixture with the product of methylation of 1,3-dimethyl-5-methoxyindoline-2-one.

4) 1,3,3-Trimethyl-5-hydroxyindoline (VII)

A solution of 1.75 g 1,3,3-trimethyl-5-methoxyindoline hydrochloride in 9 ml (50%) hydrobromic acid is heated for 1 1/2 hours on a metal bath at 140-150° in an atmosphere of oxygen-free nitrogen. After distilling off the hydrobromic acid in vacuum, the residue crystallizes. It is washed with cold alcohol. Yield 1.93 g (98.3%) hydrobromide of 1,3,3-trimethyl-5-hydroxyindoline with m.p. 211-212°. After recrystallization from absolute alcohol the m.p. is 212.0-212.5°.

3.090 mg substance: 5.180 mg CO_2; 1.830 mg H_2O. 2.950 mg substance: 5.550 mg CO_2; 1.700 mg H_2O. 2.510 mg substance: 0.127 ml N_2 (22°, 730 mm). 4.560 mg substance: 0.225 ml N_2 (22°, 734 mm). Found %: C 51.28, 51.30; H 6.63, 6.45; N 5.62, 5.51. $C_{11}H_{16}ONBr$. Calculated %: C 51.15; H 6.25; N 5.42.

The base is separated from the hydrobromide with sodium bicarbonate and is extracted with ether. The residue after elimination of the ether is purified by two sublimations at 0.5 mm and the temperature of a metal bath reaching 130°. 1,3,3-Trimethyl-5-hydroxyindoline is obtained in 88% yield, m.p. 109°.

3.170 mg substance: 8.630 mg CO_2; 2.350 mg H_2O. 3.035 mg substance: 8.310 mg CO_2; 2.350 mg H_2O. 3.730 mg substance: 0,274 ml N_2 (22°, 731 mm). 3.695 mg substance: 0.274 ml N_2 (24°, 724 mm). Found %: C 74.25, 74.19; H 8.30, 8.61; N 8.18, 8.12. $C_{11}H_{15}ON$. Calculated %: C 74.53; H 8.54; N 7.90.

The picrate is obtained in alcoholic solution and is recrystallized from alcohol. Yellow needles with m.p. 161-162°; its mixture with the picrate of 1,3,3-trimethyl-5-methoxyindoline has m.p. 132-133°.

The hydrochloride is prepared by passing hydrogen chloride into a concentrated alcoholic solution of the base. After recrystallization from absolute alcohol, it has m.p. 238-239°; its mixture with the hydrochloride of 1,3,3-trimethyl-5-methoxyindoline has m.p. 188-191°.

5) Methylurethane of 1,3,3-Trimethyl-5-hydroxyindoline (I)

To a solution of 0,91 g (1 mole) 1,3,3-trimethyl-5-hydroxyindoline in 25 ml absolute alcohol is added 1 mg sodium and, after cessation of evolution of hydrogen, 0,5 g (1.70 moles) methylisocyanate [4] in 5 ml ether. After standing for 72 hours at room temperature, the ether is distilled off and the residue washed with methanol and ether. Yield 1.08 g (90%) methylurethane of 1,3,3-trimethyl-5-hydroxyindoline with m.p. 141-142°. Recrystallization from ether-methanol raises the m.p. to 144.5-145°.

2.290 mg substance: 7.080 mg CO_2; 1.930 mg H_2O. 3.025 mg substance: 7.400 mg CO_2; 2.050 mg H_2O. 2.175 mg substance: 0.235 ml N_2 (22°, 726 mm). 2.315 mg substance: 0.250 ml N_2 (24°, 724 mm). Found %: C 66.58, 66.72; H 7.45, 7.58; N 11.94, 11.82. $C_{13}H_{18}O_2N_2$. Calculated %: C 66.63; H 7.74; N 11.96.

The picrate is prepared in alcoholic solution; m.p. 156-157° after recrystallization from alcohol.

The hydrochloride is prepared from an ethereal solution of the base and an alcoholic solution of hydrogen chloride. It crystallizes from alcohol in colorless needles with m.p. 174-175°.

3.070 mg substance: 6.495 mg CO_2; 2.025 mg H_2O. 3.025 mg substance: 6.400 mg CO_2; 1.900 mg H_2O. 2.680 mg substance: 0.255 ml N_2 (20°, 731 mm). 2.870 mg substance: 0.264 ml N_2 (20°, 731 mm). Found %: C 57.70, 57.70; H 7.38, 7.03; N 10.66, 10.31; $C_{13}H_{19}O_2N_2Cl$. Calculated %: C 57.65; H 7.08; N 10.35.

The methiodide is prepared from a concentrated solution of the base in dry acetone and excess of methyl iodide. After recrystallization from absolute alcohol the compound has m.p. 194-195° (with decomposition).

6) N-Methyl-p-phenetidide of α-Bromo-n-butyric Acid (VIII)

To a solution of 154 g (2.01 moles) N-methyl-p-phenetidine in 400 ml absolute benzene is added, with stirring and ice cooling, 117 g (1 mole) α-bromo-n-butyryl bromide. The mixture is stirred for 1/2 hour at room temperature and then for one hour with heating on the water bath. After cooling, the solution is washed with water and dilute (1:20) hydrochloric acid, and the benzene is distilled off in vacuum. The residue crystallizes completely when rubbed in the cold. The yield of N-methyl-p-phenetidide of α-bromo-n-butyric acid is nearly quantitative. Colorless crystals (from aqueous methanol) with m.p. 71-72°.

3.185 mg substance: 6.050 mg CO_2; 1.700 mg H_2O. 4.855 mg substance: 0.201 ml N_2 (25°, 730 mm). 3.720 mg substance: 0.147 ml N_2 (25°, 730 mm). Found %: C 51.80; H 5.97; N 4.55, 4.35. $C_{13}H_{18}O_2NBr$. Calculated %: C 51.97; H 6.04; N 4.66.

The combined aqueous solutions are made alkaline and yield 74.4 g (97%) of the original N-methyl-p-phenetidine with b.p. 135-138° at 19 mm.

7) 1-Methyl-3-ethyl-5-hydroxyindoline-2-one (IX)

To the technical N-methyl-p-phenetidide of α-bromo-n-butyric acid obtained in the preceding experiment is added, with stirring, 130 g (1.92 moles) sublimed aluminum chloride. After cessation of violent evolution of ethyl chloride, a further 100 g (1.48 moles) aluminum chloride is added and the reaction mixture heated for an hour at 180°, the stirring being resumed as soon as this appears feasible. The hot melt is poured onto a marble slab; on cooling it is finely pulverized and decomposed with crushed ice. The resultant slurry-like product gradually solidifies. It is washed with water and dried. Yield 89 g (92%) grey powder of 1-methyl-3-ethyl-5-hydroxyindoline-2-one with m.p. 140-145°. Colorless crystals are obtained after two recrystallizations from methanol with carbon, m.p. 175-176°.

3.195 mg substance: 8.095 mg CO_2; 1.995 mg H_2O. 5.010 mg substance: 0.343 ml N_2 (21°, 727.6 mm). Found %: C 69.09; H 6.98; N 7.60. $C_{11}H_{13}O_2N$. Calculated %: C 69.10; H 6.80; N 7.33.

8) 1-Methyl-3-ethyl-5-methoxyindoline-2-one (X)

The filtered solution of 89 g (1 mole) technical 1-methyl-3-ethyl-5-hydroxyindoline-2-one in 710 ml. 5%, potassium hydroxide solution is treated with 90 g (1.53 moles) dimethyl sulfate in the conditions described for the preparation of 1-methyl-5-methoxyindoline-2-one. Yield of 1-methyl-3-ethyl-5-methoxyindoline-2-one, 57 g (60%), b.p. 175-179° at 9 mm. For analysis the substance with b.p. 176° at 9 mm was taken.

n_D^{20} 1.5653; d_{20}^{20} 1.166; MR_D 57.33; Calc. 57.41.

5.180 mg substance: 0.353 ml N_2 (18°, 740.5 mm). 5.340 g sub.: 0.324 ml N_2 (18°, 737 mm). Found %: N 6.96, 6.90. $C_{12}H_{15}O_2N$. Calculated %: N 6.82.

9) 1,3-Dimethyl-3-ethyl-5-methoxyindoline-2-one (XI)

a) From 1-methyl-3-ethyl-5-methoxyindoline-2-one (X). To a solution of 20 g (1 mole) 1-methyl-3-ethyl-5-methoxyindoline-2-one in 50 ml absolute alcohol and 42 g (3.03 moles) methyl iodide, stirred at 50°, is added in the course of 3 hours a solution of 4.5 g (2.01 moles) sodium in 150 ml absolute alcohol. The reaction mass is worked up in the same way as described for the synthesis of 1,3,3-trimethyl-5-methoxyindoline-2-one. Yield of 1,3-dimethyl-3-ethyl-5-methoxyindoline-2-one, 19.2 g (90%); b.p. 162-164° at 10 mm. For analysis the substance with b.p. 163° at .10 mm was taken.

n_D^{20} 1.5456; d_{20}^{20} 1.109; MR_D 62.53; Calc. 62.03.

3.025 mg substance: 7.920 mg CO_2; 2.100 mg H_2O. 5.075 mg substance: 0.294 ml N_2 (23°, 728 mm), 5.085 mg substance: 0.304 ml N_2 (24°, 722 mm). Found %: C 71.39; H 7.78; N 6.40, 6.52. $C_{13}H_{17}O_2N$. Calculated %: C 71.39; H 7.82; N 6.39.

b) From 1,3-dimethyl-5-methoxyindoline-2-one (III). In conditions similar to those described above, from 20 g (1 mole) 1,3-dimethyl-5-methoxyindoline-2-one and 50 g (3.06 moles) ethyl iodide in presence of the sodium alcoholate from 4.9 g (2.03 g-atoms) sodium and 150 ml absolute alcohol, is obtained 20.4 g (89%) 1,3-dimethyl-3-ethyl-5-methoxyindoline-2-one with b.p. 126-128° at 2.5 mm; n_D^{20} 1.5453.

10) 1,3-Dimethyl-3-ethyl-5-methoxyindoline (XII) and the Pseudo Base of 3-Methyl-3-ethyl-5-methoxy-methylindoleninium (XIII)

19.2 g (1 mole) 1,3-dimethyl-3-ethyl-5-methoxyindoline-2-one is reduced with 70 g sodium (34.7 g-atoms) in 700 ml butyl alcohol in the conditions described for the synthesis of 1,3,3-trimethyl-5-methoxyindoline. Four fractional distillations yielded 8.7 g (48%) 1,3-dimethyl-3-ethyl-5-methoxyindoline with b.p. 120-125° at 1.5 mm and 4.7 g (24%) pseudo base of 3-methyl-3-ethyl-5-methoxy-methylindoleninium with b.p. 140-150° at 1.5 mm.

The picrate of 1,3-dimethyl-3-ethyl-5-methoxyindoline crystallizes from alcohol in the form of yellow crystals with m.p. 125-126° (the mixture with picric acid melts at 90-92°).

The hydrochloride of 1,3-dimethyl-3-ethyl-5-methoxyindoline is obtained in 75% yield by adding an alcoholic solution of hydrogen chloride to a concentrated alcoholic solution of the base. Colorless crystals from alcohol with m.p. 178.0-178.5°.

5.225 mg substance: 0.274 ml N_2 (21°, 742 mm). 4.765 mg substance: 0.230 ml N_2 (19°, 753 mm). Found %: N 5.94, 5.59. $C_{13}H_{20}ONCl$. Calculated %: N 5.80.

For analysis of the pseudo base of 3-methyl-3-ethyl-5-methoxy-methylindoleninium the substance with b.p. 145-146° at 1.5 mm was taken.

5.230 mg substance: 0.279 ml N_2 (20°, 752 mm). 5.115 mg substance: 0.274 ml N_2 (20°, 752 mm). Found %: N 6.15, 6.18. $C_{13}H_{19}O_2N$. Calculated %: N 6.34.

The picrate is obtained by heating an alcoholic solution of the pseudo base with excess picric acid. Dark-yellow crystals from alcohol with m.p. 138-138.5° (with decomposition).

11) 1,3-Dimethyl-3-ethyl-5-hydroxyindoline (XIV)

A solution of 6.0 g 1,3-dimethyl-3-ethyl-5-methoxyindoline (XII) hydrochloride in 30 ml 50% hydrobromic acid is heated for 1 1/2 hours on a metal bath at 140-150° in an atmosphere of oxygen-free nitrogen. The hydrobromic acid is completely distilled off in vacuum, the solid residue is dissolved in the minimum amount of boiling alcohol and dry ether is added. On cooling, a precipitate comes down. Recrystallization from absolute alcohol gives 6.5 g (96%) hydrobromide of 1,3-dimethyl-3-ethyl-5-hydroxyindoline, m.p. 164-165°.

2.985 mg substance: 5.765 mg CO_2; 1.740 mg H_2O. 2.875 mg substance: 5.540 mg CO_2; 1.720 mg H_2O. 4.945 mg substance: 0.230 ml N_2 (23°, 730 mm). Found %: C 52.67, 52.55; H 6.52, 6.69; N 5.15. $C_{12}H_{18}ONBr$. Calculated %: C 52.93; H 6.67; N 5.15.

The base is obtained by dissolving the hydrobromide in absolute alcohol and adding an alcoholic solution of ammonia until the ammonium bromide is completely precipitated. After addition of ten times the volume of absolute ether, the solution is filtered and the solvent driven off. The residue is extracted several times with small portions of warm dry ether, the ether is driven off and the residue distilled. At 0.3-0.4 mm and the temperature of the metal bath (up to 140°), 1,3-dimethyl-3-ethyl-5-hydroxyindoline comes over in the form of a yellowish, viscous oil.

3.090 mg substance: 8.565 mg CO_2; 2.375 mg H_2O. 3.320 mg substance: 0.216 ml N_2 (24°, 733 mm). Found %: C 75.60; H 8.60; N 7.21. $C_{12}H_{17}ON$. Calculated %: C 75.34; H 8.97; N 7.32.

The picrate is prepared in alcoholic solution and is recrystallized from alcohol. Yellow crystals with m.p. 150-150.5°.

The hydrochloride is prepared by passing dry hydrogen chloride into an alcoholic solution of the base and is brought down by addition of ether. After recrystallization from alcohol, it has m.p. 174.5-175.5°; its mixture with the hydrochloride of 1,3-dimethyl-3-ethyl-5-methoxyindoline has m.p. 145-147°.

3.020 mg substance: 6.995 mg CO_2; 2.165 mg H_2O. 3.005 mg substance: 6.980 mg CO_2; 2.170 mg H_2O. 5.750 mg substance: 0.309 ml N_2 (22°, 735 mm). 4.690 mg substance: 0.265 ml N_2 (24°, 722 mm). Found %: C 63.17, 63.35; H 8.02, 8.08; N 6.01, 6.17. $C_{12}H_{18}ONCl$. Calculated %: C 63.27; H 7.97; N 6.15.

12) Methylurethane of 1,3-Dimethyl-3-ethyl-5-hydroxyindoline (II)

2.5 g (1 mole) 1,3-dimethyl-3-ethyl-5-hydroxyindoline is dissolved in 20 ml absolute ether and 1 mg sodium is added. After the latter has dissolved, 2.0 g (2.68 moles) methylisocyanate [4] in 10 ml absolute ether is stirred in and the whole left at room temperature for 48 hours. The solution is filtered from the very small flocculent precipitate and evaporated in vacuum. The residue gradually crystallizes. It is washed with a mixture of ether and ligroine (b.p. 40-60°) to give 1.98 g (61%) of a white powder – the methylurethane of 1,3-dimethyl-3-ethyl-5-hydroxyindoline with m.p. 96-98°. After recrystallization from ether it has m.p. 99-100°.

2.965 mg substance: 7.350 mg CO_2; 2.150 mg H_2O. 3.015 mg substance: 7.515 mg CO_2; 2.095 mg H_2O. 3.550 mg substance: 0.348 ml N_2 (18°, 740 mm). 3.710 mg substance: 0.360 ml N_2 (22°, 748 mm). Found %: C 67.60, 67.99; H 8.12, 7.77; N 11.15, 11.50. $C_{14}H_{20}O_2N_2$. Calculated %: C 67.70; H 8.12; N 11.28.

The picrate is prepared by the usual method and is recrystallized from alcohol. Bright-yellow crystals with m.p. 147-148°; its mixture with the picrate of the original 1,3-dimethyl-3-ethyl-5-hydroxyindoline has m.p. 126-129°.

SUMMARY

1. The synthesis is realized of the methylurethanes of 1,3,3-trimethyl-5-hydroxy indoline and of 1,3-dimethyl-3-ethyl-5-hydroxy indoline.

2. It is shown that reduction with sodium and butyl alcohol of 1,3,3-trialkyl-5-methoxyindoline-2-ones gives, apart from the corresponding indolines, the pseudo bases of 3,3-dialkyl-5-methoxy-alkylindoleniniums.

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ACADEMICIAN VLADIMIR MIKHAILOVICH RODIONOV

(On his 75th Birthday Anniversary)

M. M. Shemyakin

On October 28, 1953, the 75th birthday anniversary and the 50th anniversary of the scientific, practical and pedagogical activities of one of the most outstanding Soviet chemists – Academician Vladimir Mikhailovich Rodionov – was celebrated.

V. M. Rodionov belongs to those men who are exceptionally endowed and gifted by nature. His personality is a brilliant combination of scientist, engineer, pedagogue and social worker.

The theoretical works of V. M. Rodionov and his school bear the marks of profound scope of investigation and variety of problems studied. Within the 50-year period of his scientific activity, V. M. Rodionov has extended his investigations in the organic chemical field to such diverse types as aliphatic, alicyclic, aromatic and heterocyclic series, relative to dyes, alkaloids, pharmaceuticals, vitamins and perfumes. In particular, V. M. introduced much that is new, valuable and original into the field of β-amino acids, into pyrimidine and imidazole chemistry and other heterocyclic compounds, as well as the chemistry of aromatic compounds, in particular, of aldocarboxylic acids. Discovered and developed in detail were successful procedures for the alkylation of organic compounds, an original method for introducing the diazo group into phenols, quite ingenious in its simplicity of method, methods of synthesizing β-amino acids and their analogues, and procedures for converting β-amino acids and their derivatives into various types of heterocyclic compounds, which are widely known. Of excellent caliber was V. M.'s investigation on the mechanism of the Hofmann degradation of carboxylic acid amides. Of added interest are the possibilities opened up by V. M. for utilization of this reaction for synthetic purposes, in particular, for the derivation of certain types of heterocyclic compounds. The fundamental investigations of V. M. in β-amino acid chemistry, carried out in 1946, were honored by the 1st order Stalin prize. The extensive works of V. M. in the chemistry and technology of organic intermediates and dyes, which have been extensively applied in the industry, were also honored by the Stalin prize in 1949 and in 1950. V. M. Rodionov has assembled many students and co-workers, and has created a large school, the labors of which are a valuable heritage of science and technology. He has published about 180 works on various problems of chemistry, technology and economics, has published a series of interesting reviews, and has written many articles on the works and life activities of prominent Russian and Soviet scientists.

Being both an researcher and an engineer at the same time, and having always been closely related to various branches of the chemical industry, V. M. Rodionov in his active period has invariably aimed at combining his theoretical research with the practical needs of socialist development. A number of his works in the fields of alkaloids, pharmaceuticals, organics, intermediates, dyes and aromatic substances were directed toward solutions of actual problems of immediate interest to industry, and many developed methods for synthesizing organic compounds were put into production by his direct participation. V. M. Rodionov is one of the founders and first leaders of the national aniline dye and pharmaceutical industries. At the present time he continues to take an active part in development of the chemical industry, having been for many years assistant to the Chairman of the Technical Soviet Ministry of Chemical Industry, visiting plants, consulting with industrial workers, and carrying out with them a number of joint investigations. Recently, V. M. has given particular attention to development of the synthetic aromatic industry.

The social and scientific-organizational activities of V. M. Rodionov are also quite versatile. For many years he has actively participated in work of the D. I. Mendeleev All-Union Chemical Society, being first chairman of the section, then vice-president, and finally president of the society. He has also devoted considerable attention to scientific-organizational work in the Academy of Sciences of the USSR. V. M. particpates actively in various scientific and technical conferences, delivering reports and in discussions. It is sufficient to mention that within the past few years he has particpated in numerous conferences held in Moscow, Leningrad, Kiev, Erevan, Tashkent, Irkutsk, Kuznetsk and other cities. V. M. is an editor and member of the editorial boards of several scientific journals and scientific-technical publications. For many years he has been a member of the Expert Commission on Chemistry of the VAK (Ministry of Culture). All who are acquainted with V. M. Rodionov hold him in great esteem, praising him highly for his exceptional knowledge and experience, his principles and his inexhaustible initiative and energy.

We should linger upon one more side of V. M. Rodionov's activities – his pedagogical work, which began at the Moscow Higher Technical School, and which has continued uninterrupted up to the present time at various institutions of higher learning in Moscow. At first he gave lecture courses in pharmaceutical chemistry and the chemistry of alkaloids, which were synthesized in an interesting manner, and later he lectured in courses on the chemistry and chemical technology of dyes and intermediates, and for the past decade and a half – courses in organic chemistry. V. M.'s lectures are simple and clear in outline, always of profound subject matter, and interesting; in them he propounds not only the bases of theoretical concepts, but also the principal veins of creative thought by investigators, and reflects upon all of the important achievements of science and technology, imparting to them his large, accumulated experience in scientific and practical matters. V. M. always devotes much of his attention and powers to leadership of the scientific work of the undergraduate and graduate students, and of his numerous co-workers Of exceptional erudition, and being possessed of an excellent memory, being interested, and following continuously developments in various branches of chemistry and chemical technology, as well as being, himself, an excellent experimenter, V. M. is found to be an outstanding leader and teacher for young, scientific workers. He behaves as an elder colleague with both co-workers and students alike. He knows how to discover and to develop able students, giving them always the opportunity to develop their abilities. With his authority he does not suppress the initiative of young scientific workers, but helps them through advice and by sharing experiences with them, which unquestionably contributes to their growth and to their emergence into the scientific field. V. M. Rodionov has educated hundreds of engineers and investigators who, at the present time, occupy leading positions in industry, in institutions of higher learning, and in research institutes. Many of his pupils have already created their own scientific approaches and schools.

V. M. Rodionov is not only a great scientist, but also a charming and sensitive man. All who have met him in their lifetime know well his kindness and responsiveness, his affability and directness in dealing with people. From the first moments of being in his company, all feel entirely at ease, as though they had known him for many years, and feel a kinship with him. One can approach him with any problem and he is always ready to respond, will try to help with advice and action whether the problem is scientific or personal. Nonetheless, as a man of high principles, and considering honesty in people and in himself above all, V. M. with all of his charm can, when necessary, be severe and rigid. However, he usually establishes friendly relationships with his pupils and co-workers for many years. V. M. displays lively interest in their works and takes sincere pleasure in their creative success and achievements in science. V. M. loves his science deeply and knows how to inject into his pupils an objective love for it.

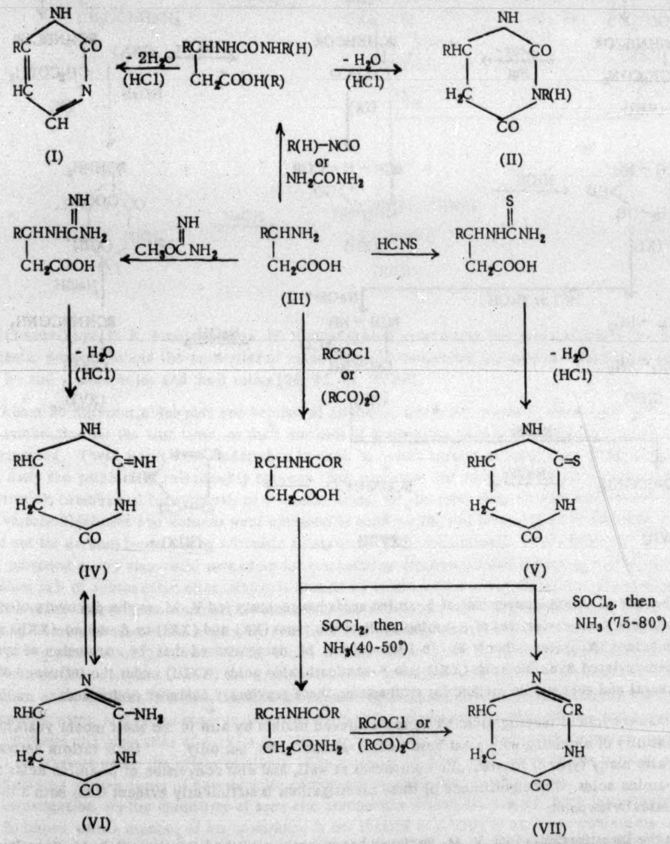
When speaking of V. M. Rodionov, there should not be forgotten another rare and valuable characteristic. The brilliance of his thought, the keenness of his mind, the inexhaustible love of scientific creation, the diversity of his interests – all of this remains unchanged and forces us to forget his age. Lately V. M. Rodionov has expanded his investigations on a particularly broad scale of most diverse fields; within the past 5 years, he has published about 70 articles on various organic chemistry problems which are of considerable theoretical and practical interest. This research requires more detailed illustration.

As in preceding years, V. M. Rodionov, together with a number of his pupils and co-workers (V. G. Avramenko, L. V. Antik, N. N. Bezinger, T. K. Veselovskaya, V. K. Zvorykina, V. V. Kiseleva, T. S. Kiseleva, N. A. Kravchenko, B. I. Kurtev, O. S. Urbanskaya, A. M. Fedorova, E. I. Chukhina, E. V. Yavorskaya, N. G. Yartseva and others), has paid particular attention to β-amino acid chemistry, and in particular, to methods for their conversion to various types of heterocyclic compounds [1-22]. All of these investigations of V. M. have created considerable interest, particularly since certain β-amino acids, as well as heterocyclic compounds resulting from them, enter into the composition of many biologically-active natural and synthetic compounds – antibiotics, vitamins, nucleic acids, pharmaceutical preparations, and others.

During the period 1948-1953, V. M. Rodionov has extended considerably the field of application of the method which he discovered in 1926 for synthesizing β-amino acids; synthesis of a number of new β-amino acids and their various derivatives has been realized by this method, the effects of structural and external factors during the course of their formation have been studied, the validity of the reaction mechanism earlier proposed has been confirmed, and optimal conditions for carrying out the reaction have been worked out. At the present time, the V. M. Rodionov method has become the most popular, and no doubt best, procedure for synthesizing various β-amino acids, their derivatives, and analogs, synthetic yields of which, in many cases, have reached as high as 70 %.

In continuing means of investigating β-amino acid conversions into various heterocyclic compounds, V. M. has recently also studied in a number of cases the possibility of transition from β-amino acids (III) to substituted di-, tetra- and hexahydropyrimidines of the type (I), (II) and (VII), observed earlier by him, and at the same time has developed new synthetic procedures for substituted hexahydropyrimidines of types (V) and (IV) ⇌ (VI) (see scheme 1). A thorough study of the conditions of these reaction processes made it possible finally for V. M. to develop very simple, and in many cases general, methods for synthesis of substituted pyrimidines of the type enumerated above.

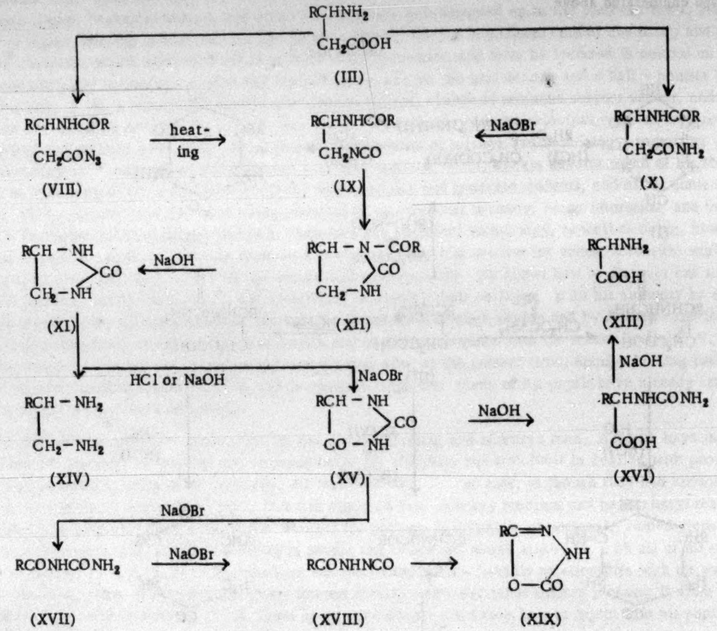
Scheme 1



(I)
- 2H₂O (HCl)
RCHNHCONHR(H) CH₂COOH(R)
- H₂O (HCl)
(II)
R(H)–NCO or NH₂CONH₂
RCHNHC(=NH)NH₂ CH₂COOH
CH₃OC(=NH)NH₂
RCHNH₂ CH₂COOH
(III)
HCNS
RCHNHC(=S)NH₂ CH₂COOH
- H₂O (HCl)
RCOCl or (RCO)₂O
- H₂O (HCl)
(IV)
RCHNHCOR CH₂COOH
(V)
SOCl₂, then NH₃(40-50°)
SOCl₂, then NH₃ (75-80°)
(VI)
RCHNHCOR CH₂CONH₂
RCOCl or (RCO)₂O
(VII)

Of no less value are methods for synthesis of substituted glyoxylidones of the type (XI) and (XII) which were discovered and developed in detail by V. M., and which previously had been found to be relatively or completely unavailable substances. A variety of representatives of these two types of heterocyclic compounds can at present be readily obtained from β-amino acids by the following procedures: (III) ⟶ (VIII) ⟶ (IX) ⟶ (XII) ⟶ (XI) or (III) ⟶ (X) ⟶ (IX) ⟶ (XII) ⟶ (XI) (see Scheme 2). A thorough study of the latter reaction carried out quite recently by V. M. has led to very interesting results. He has demonstrated the feasibility of converting β-amino acids not only into glyoxylidones (XI) and (XII), but also into other types of heterocyclic compounds – hydantoins (XV) and hydroxydiazolones (XIX); moreover, there was found the possibility for a very original and at the same time simple conversion of β-amino acids (III) to α-amino acids (XIII). The mechanism for all of these complex conversions presented in Scheme 2 has been experimentally confirmed, and at the present time is found to be proved correct. These exceptionally fine works of V. M. characterize splendidly the profoundness and intricacy of his experimental and theoretical research.

Scheme 2



RCHNH₂ CH₂COOH
(III)
RCHNHCOR CH₂CON₃
(VIII)
heat-ing
RCHNHCOR CH₂NCO
(IX)
NaOBr
RCHNHCOR CH₂CONH₂
(X)
RCH−NH CH₂−NH CO
(XI)
NaOH
RCH−N−COR CH₂−NH CO
(XII)
RCHNH₂ COOH
(XIII)
NaOH
HCl or NaOH
NaOBr
RCH−NH₂ CH₂−NH₂
(XIV)
RCH−NH CO−NH CO
(XV)
NaOH
RCHNHCONH₂ COOH
(XVI)
NaOBr
RCONHCONH₂
(XVII)
NaOBr
RCONHNCO
(XVIII)
RC=N NH O−CO
(XIX)

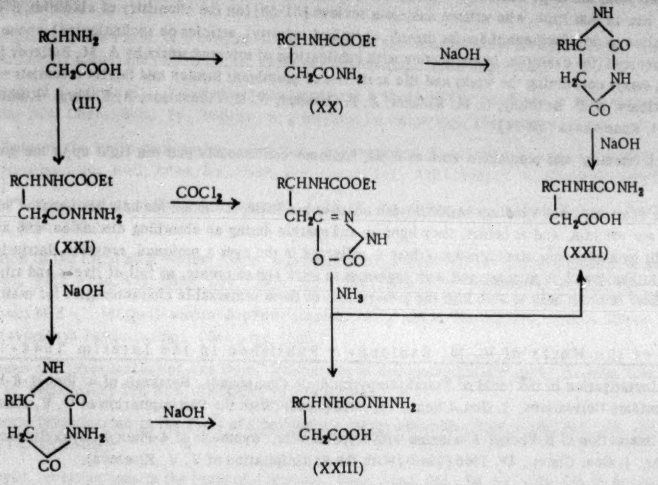
A thorough study of various conversions of β-amino acids has recently led V. M. to the discovery of specific means of transition from derivatives of β-amino acids of the types (XX) and (XXI) to β-ureido-(XXII) and to β-semicarbazido acids (XXIII) (see Scheme 3). In 1952-1953 V. M. demonstrated that the conversion of hydrazides of N-carboethoxylated β-amino acids (XXI) into β-semicarbazido acids (XXIII) under the influence of caustic alkali is a general and very simple method for synthesizing these previously unknown compounds.

This remarkable cycle of investigations by V. M., achieved mainly by him in the most recent years, has established the feasibility of obtaining with great ease from β-amino acids, not only their various derivatives and analogs, but also many types of heterocyclic compounds as well, and also conversion of β-amino acids to the corresponding α-amino acids. The significance of these investigations is sufficiently evident from both a theoretical and a practical viewpoint.

Along with the investigations cited, V. M. Rodionov has recently published, jointly with B. M. Bogoslovsky, M. A. Gubareva, Z. S. Kazakova, N. N. Suvorov, A. M. Fedorova, M. G. Chentsova and L. V. Shagalov a series of interesting works [23-32] pertaining to a study of synthetic procedures, as well as the properties of various heterocyclic compounds which are derivatives of pyrazolone, imidazole, indole, thionaphthene, tetrrahydroisoquinoline and benzophenanthridine. Synthesis of this latter type was undertaken in connection with a study of synthetic methods for chelidonine – an alkaloid contained in celandine (Chelidonium majus).

For the past five years, V. M. Rodionov, with a number of coworkers (V. N. Belov, R. Sh. Grigoryeva, T. S. Kiseleva, S. A. Kore, I. V. Machinskaya, G. I. Moldivanskaya, E. A. Ogorodnikova, E. F. Polunina, K. S. Polyakova,

Scheme 3



E. L. Simanovskaya, E. K. Smolyaninova, N. N. Shevyakova and others), has paid considerable attention to a study of synthetic procedures and the properties of many carbonyl-containing compounds: aldehydes, ketones, γ-diketones, β- and γ-keto acids and their esters [26, 27, 31, 33-49].

About 30 different aldehydes and ketones of aliphatic, alicyclic, aromatic and heterocyclic series have been either synthesized for the first time, or their methods of preparation have been substantially modified and considerably improved. These works were undertaken in order to obtain various carbonyl-containing aromatic substances and to study the problem of relationship between their structures and aroma, as well as to have readily accessible raw materials (aldehydes) for synthesis of β-amino acids. Of the total research work carried out, a considerable number of various aldehydes and ketones were obtained in good yields, and several general synthetic procedures were worked out for carbonyl-containing aromatic substances. Thus, for example, V. M. Rodionov, V. N. Belov, and others, proposed a very successful procedure for synthesizing monosubstituted acetoacetic acid esters directly from the sodium salt of acetoacetic ester, which is formed by condensation of ethyl acetate; this method is of great technological value for perfume manufacture since it is possible in principle to develop simple synthetic means for producing a series of substituted aldehydes (via the corresponding ketones and esters of glycidic acids).

Among other investigations of V. M. which are devoted to works on carbonyl-containing compounds, there should be mentioned works in which are described a new method for synthesis of γ-diketones (from α-haloketones and sodium acetoacetate), a simple method for converting acetoacetic ester into nitroacetic ester (through isonitrosoacetoacetic ester, and its subsequent oxidation by H_2CrO_4), the properties of γ-chloro- and α,γ-diphenylacetoacetic esters, synthesis and properties of δ-chlorolevulinic acid, and the transformations of cotarnine, hydrastinine and their benzoyl derivatives under the effect of alkali. The majority of these works were for the purpose of finding methods for synthesizing various types of heterocyclic compounds as mentioned briefly above.

Investigation on the chemistry of aromatic compounds, which has recently been intensively developed by V. M. Rodionov with a number of his coworkers, is not limited to a study of carbonyl-containing compounds only. Syntheses of other types of substances – aromatic and alicyclic hydrocarbons, phenols, alcohols, esters and others – have also been achieved. In this connection, isopropylation and isobutylation processes for benzene and phenols, reactions of partial and exhaustive hydrogenation of benzanthrone, and certain other conversions have been thoroughly studied [39, 41-43, 45, 47, 49, 50].

The research field covered by V. M. Rodionov has widened and expanded our knowledge of the chemistry of carbonyl-containing, and other types of organic compounds, but to a particular degree has favored the creation of a series of standard procedures for synthesizing aromatic substances, making it possible to realize the synthesis of many compounds valuable in perfume manufacture, and has provided an opportunity for discovering certain relationships between the structure of organic molecules and their odors.

Apart from the large number of experimental papers which V. M. Rodionov has published over the past several years, he has, in that time, also written numerous reviews [51-55] (on the chemistry of alkaloids, β-amino acids, and dyes, relative to development of Soviet organic chemical industry), articles on technological-economic problems [57-58], reviews (for example, in connection with publications of selected works by A. M. Butlerov [56]), and biographical essays concerning the works and life activities of prominant Russian and Soviet scientists – D. I. Mendeleev, A. M. Butlerov, N. D. Zelinsky, N. M. Kizhner, A. P. Orekhov, N. N. Vorozhtsov, A. E. Porai-Koshits, A. M. Berkengeim, S. I. Kanevskaya [59-64].

Such intensive and productive work as V. M. Rodionov continuously puts out right up to the present must be admired.

The years pass, but Vladimir Mikhailovich changes but little. Although his hair has become white, his eyes as before are youthful, and as before, they light up and sparkle during an absorbing discussion, and as before, the eyes are lit by a keen, questioning mind, or there is reflected in the eyes a profound, creative, intrinsic activity. Vladimir Mikhailovich is so consumed with eagerness to work and to create, so full of lively and stimulating energy, that there remains only to wish him the preservation of these remarkable characteristics for many years to come.

Listing of the Works of V. M. Rodionov, Published in the Interim 1948-1953.*

1. Investigation in the Field of Tetrahydropyrimidinic Compounds. Synthesis of 4-Phenyl-6-hydroxytetrahydropyrimidine Derivatives. J. Gen. Chem., 18, 1912 (1948) (With the Participitation of V. V. Kiseleva).

2. Interaction of β-Phenyl-β-alanine with Hypobromite. Synthesis of 4-Phenyl Glyoxylidone and Its Acyl Derivatives. J. Gen. Chem., 18, 1905 (1948) (With the Participitation of V. V. Kiseleva).

3. Investigation in the Field of β-Amino Acids. Synthesis of β-Guanidino Acids and Their Conversion to Hexahydropyrimidines. J. Gen. Chem., 18, 2023 (1948) (O. S. Urbanskaya Participating).

4. Conversion of β-Alkyl-(Aryl)-β-N-carbethoxyaminopropionic Acid Amides into β-Ureido Acid. Proc. Acad. Sci. 65, 853 (1949) (V. K. Zvorykina Participating).

5. Interaction between Amino Acid Hydrochlorides and Ethylene Oxide. Bull. Acad. Sci., USSR, Div. Chem. Sci. 108 (1950), (N. G. Yartseva Participating).

6. Structure of 1-Naphthaldehyde-8-carboxylic Acid. Bull. Acad. Sci. USSR, Div. Chem. Sci., 247 (1950) (A. M. Fedorova Participating).

7. Condensation Reaction of Py-Indolealdehydes with Malonic Acid and with Cyanoacetic Ester. J. Gen. Chem., 20, 2202 (1950) (T. K. Veselovskaya Participating). [See page 2287]**

8. New Data on the Hofmann Reaction. Article III. Interaction of Acylated Amides of β-Aminopelargonic Acid with Alkaline Hypobromites. Bull. Acad. Sci. USSR, Div. Chem. Sci., 608 (1950) (V. K. Zvorykina Participating).

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10. Synthesis and Characterization of β-(β-Naphthyl)-β-aminopropionic Acid and Some of Its Derivatives. Bull. Acad. Sci. USSR, Div. Chem. Sci., 113 (1952) (B. I. Kurtev Participating). [See page 123.]

11. β-(β-Naphthyl)-β-aminopropionic Acid and Its Pyrimidine Derivatives. Bull. Acad. Sci. USSR, Div. Chem. Sci., 268 (1952) (B. I. Kurtev Participating). [See page 285].

12. Synthesis and Characterization of β-(α-Naphthyl)-β-aminopropionic Acid. Proc. Acad. Sci., 82, 269 (1952) (N. A. Kravchenko Participating).

13. Synthesis of β-(Cyclohexyl)-β-aminopropionic Acid and Some of Its Derivatives. Bull. Acad. Sci. USSR, Div. Chem. Sci., 278 (1952) (T. S. Kiseleva Participating). [See page 293].

14. A New Synthesis of Alkyl Esters of β-Amino Acids. Bull. Acad. Sci. USSR, Div. Chem. Sci., 696 (1952) (N. N. Bezinger Participating). [See page 637.]

15. The Curtius Reaction with a Series of β-Amino Acids. Bull. Acad. Sci. USSR, Div. Chem. Sci., 962 (1952) (N. N. Bezinger Participating). [See page 847.]

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*A list of the earlier works of V. M. Rodionov can be found in J. Gen. Chem., 18, 1894 (1948) and in Chem. Prog. 17, 543 (1948).

** Here, and subsequently in this listing, numbers in brackets indicate the pagination of the Consultants Bureau English Translation of the paper listed.

16. A General Procedure for Synthesis of β-Semicarbazido Acids. Proc. Acad. Sci., 85, 579 (1952) (V. K. Zvorykina Participating).

17. Investigation in the Field of β-Amino Acids. Synthesis and Conversions of β-Aminobutyric Acid. Bull. Acad. Sci. USSR., Div. Chem. Sci., 103 (1952) (N. G. Yartseva Participating). [See page 113].

18. Synthesis of 5-Alkylated 1,3,4-Hydroxydiazolones and A Study of Their Interaction with Ammonia. Bull. Acad. Sci. USSR, Div. Chem. Sci., 70 (1953) (V. K. Zvorykina Participating). [See page 61].

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20. On the Characteristics of Phthalimidineacetic Acid. J. Gen. Chem., 23, 396 (1953) (E. I. Chukhina Participating). [See page 403.]

21. Research in the Field of β-Amino Acids. Synthesis of β-(β-Decalyl) -β-amino Propionic Acid and its Characterization. Bull. Acad. Sci. USSR, Div. Chem. Sci., 253 (1953) (L. V. Antik Participating). [See page 231].

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23. Synthesis and Investigation of Azo Dyes. Derivatives of 3-Hydroxythionaphthene. J. Appl. Chem., 21, 962 (1948) (B. M. Bogoslovsky and Z. S. Kazakova Participating).

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28. A New Method for Formation of Thioindigo on Fiber. J. Appl. Chem., 22, 670 (1951) (B. M. Bogoslovsky and Z. S. Kazakova Participating). [See page 757].

29. New Data in the Field of Chemistry of Pyrazolone Derivatives. Bull. Acad. Sci. USSR, Div. Chem. Sci., 1049 (1952) (A. M. Fedorova Participating). [See page 917].

30. Synthesis of 6-Carboxy-11-methyl-5,6,13,14-tetrahydro-1,2-benzophenanthridine. Proc. Acad. Sci., 82, 731 (1952) (N.N. Suvorov and L. V. Shagalov Participating).

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33. Synthesis of α-Nitrosubstituted Carboxylic Acid Esters. Article I. Nitroacetoethyl Ester. J. Gen. Chem., 18, 917 (1948) (I. V. Machinskaya and V. M. Belikov Participating).

34. New Synthesis of γ-Diketones. Proc. Acad. Sci., 68, 535 (1949) (E. F. Polunina Participating).

35. Synthesis of Phthalide from Phthalic Anhydride. J. Appl. Chem., 22, 853 (1949) (E. I. Chukhina Participating).

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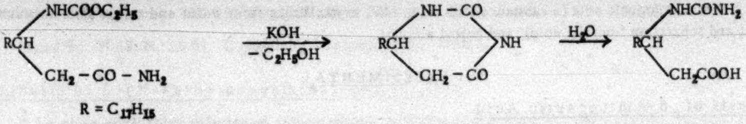
β-AMINOCAPRIC ACID AND ITS CONVERSIONS

V. M. Rodionov, V. K. Zvorykina and N. E. Kozhevnikova

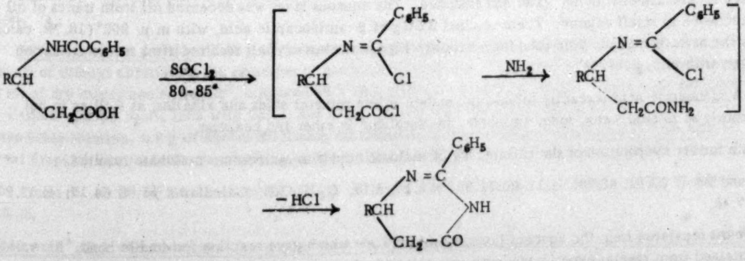
β-Aminocapric acid and 4-heptyl-2,6-dihydroxyhexahydropyrimidine have been synthesized by K. Lang and F. Addickes [1]. The authors succeeded in determining the presence of dihydrouracil in the urine of experimental animals while feeding a diet containing β-amino acids.

Having extended β-amino acid syntheses according to Rodionov from new aldehydes of the aliphatic series, the present authors have undertaken the problem of obtaining new homologs of β-amino acids and of confirming common reactions found for β-amino acids by the authors.

The following derivatives of β-aminocapric acid were synthesized: β-carboethoxy- derivative, its amide, the N-benzoyl derivative and its amide and the β-ureido acid. The latter was obtained by both the usual method by reacting β-aminocapric acid with potassium cyanate, and also by heating with 5% KOH, a solution of β-(N-carboethoxy)-aminocapric acid amide, i.e., according to a reaction established for the first time by the authors, using β-(N-carboethoxy)aminopelargonic acid amide as an example, and verified on a series of other β-amino acids [2].

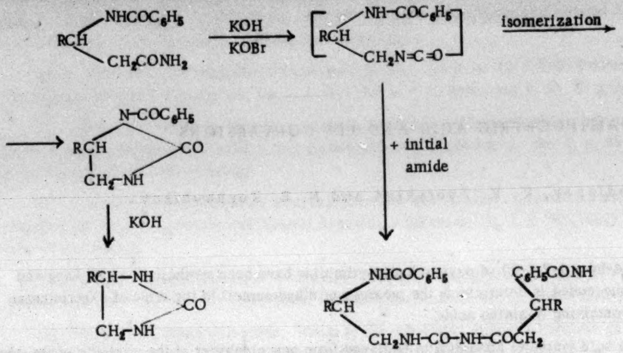


2-Phenyl-4-heptyl-6-hydroxytetrahydropyrimidine was synthesized according to the thionyl chloride method which is standard for benzoyl derivatives of β-amino acids [3] which have been synthesized so far:



By reacting an alkaline hypobromite solution with the benzoyl amide derivative of β-aminocapric acid, it was possible to isolate four substances: 5-heptylglyoxalidone, 1-N-benzoyl-5-heptylglyoxalidone, benzoic acid, and a substance with m.p. 216°, which, according to elementary analysis data, was found to be a urea derivative. On the basis of products isolated, it was possible to deduce that the reaction proceeds in the following manner (see top of following page).

Formation of 1-N-benzoyl-5-heptylglyoxalidone (product of the intramolecular isomerization of the isocyanic ester) during this reaction again confirmed the correctness of the scheme proposed by the authors [4].



To verify the structure of 1-N-benzoyl-5-heptylglyoxalidone, its hydrolysis was carried out with 20% KOH solution. 5-Heptylglyoxalidone and benzoic acid were isolated.

As side-products in the synthesis of β-aminocapric acid, an unsaturated acid with an equivalent weight of 264 (evidently a mixture of decylenic acid and heptylbutyrolactone), and caprylic acid, were separated. Formation of caprylic acid should be related to a partial disproportionation of the initial aldehyde. Feasibility of a similar reaction was earlier observed during the synthesis of β-aminopelargonic acid, wherein it was possible to isolate both products of the aldehyde disproportionation: enanthic acid in the form of its compound with a molecule of β-aminopelargonic acid (a substance with m.p. 140°, crystallizing from water and stable after dissolution in alkali and separation from the acid), and heptyl alcohol.

EXPERIMENTAL

Synthesis of β-Aminocapric Acid

22 ml of 8.1% alcoholic NH_3 solution was added with cooling (ice and salt) to 12 g of octanal, the mixture cooled for 30 minutes, and 9.75 g of finely powdered malonic acid then introduced with stirring. The flask was connected with descending condenser and then heated for 1.5 hours at 70°, followed by 7 hours on a boiling water bath. A transparent yellow oil resulted, from which, upon cooling, crystals separated. The condensation product was treated several times with hot water and siphoned. The aqueous layer was decanted off from traces of oil and concentrated to small volume. There resulted 2.25 g of β-aminocapric acid, with m.p. 202° (18.7%, calculating on the basis of malonic acid used for reaction). Fine, colorless crystals resulted after recrystallization from water, with m.p. 205-206°.

β-Aminocapric acid is readily soluble in alcohol, dilute mineral acids and alkalies, as well as in hot water – poorly so in cold water, soda, ammonia, and insoluble in ether and benzene.

With further evaporation of the filtrate, 3 g of malonic acid plus ammonium malonate resulted.

Found %: C 63.81, 63.90; H 11.46, 11.31; N 8.17, 8.14. $C_{10}H_{21}O_2N$. Calculated %: C 64.17; H 11.20; N 7.48.

The oil separated from the aqueous layer – about 3.7 g – which gave reaction for double bond. By washing the oil obtained from several experiments with soda solution, the acid was isolated as a light-yellow oil.

0.127, 0.1083 g substance: Used for titration: 7.5, 6.3 ml KOH (T = 0.004882). Equivalent weight found: 138.7, 140.8. $C_8H_{16}O_2$. Equivalent weight calculated: 144.

Synthesis of the Amide. 0.71 g of the acid and 0.49 g of thionyl chloride were heated at 40° for 3 hours. The reaction product was soluble in ether and in saturated NH_3. After distilling off the ether, there resulted a partially crystallized oil. The crystals were filtered off and recrystallized from water. Scaly platelets with m.p. 94-96° (m.p. 105-106° according to the literature data).

Found %: N 9.91. $C_8H_{17}ON$. Calculated %: N 9.78.

After washing with soda, the oil was dissolved in ether and treated with 10% NaOH. Traces of oil were separated from the alkaline solution. ~~After alkali, the~~ ether solution was washed several times with water. Part of the oil from the ether layer went into the wash waters. Upon acidification, oil separated, which was extracted with ether; the ether solution was washed three times with water, dried with Na_2SO_4 and distilled. A yellow, transparent oil resulted, giving a reaction for double bond.

0.0873, 0.1254 g substance: Used for titration: 2.7, 3.9 ml KOH. Equivalent weight found: 264.8, 263.8. $C_{10}H_{18}O_2$. Equivalent weight calculated: 170.

A large equivalent weight indicated presence of lactone in the acid isolated.

Synthesis of β-Ureidocapric Acid

1 g of β-aminocapric acid was dissolved, with heat, in 40 ml of water. 0.5 g of potassium cyanate was added, with cooling, and heating then carried out for 4 hours on a rapidly boiling water bath. The slightly turbid solution was filtered off and acidified to Congo red with HCl and with efficient cooling. The resulting white crystalline precipitate was filtered off, washed with water and dried. 0.8 g (65%) of crystals resulted, with m.p. 125-127°. After recrystallization from hot water, there resulted colorless needles: 0.12 g with m.p. 129-130°, and 0.61 g from the mother liquor, with m.p. 122-127°.

Found %: C 57.2, 57.18; H 9.74, 9.63; N 12.10, 12.00. $C_{11}H_{22}O_3N_2$. Calculated %: C 57.39; H 9.56; N 12.17.

Synthesis of 4-Heptyl-2,6-dihydroxyhexahydropyrimidine

0.6 g of β-ureidocapric acid was heated for 1 hour on a wire gauze with 10 ml of HCl (1: 1). Upon cooling a white precipitate separated from the solution in the form of long, thin needles. The precipitate was filtered off, washed with a small amount of water, and recrystallized from dilute alcohol (4: 1). There resulted 0.4 g of long, colorless needles with m.p. 181-182° (yield 72.3% of theory).

Found %: N 13.38, 13.51. $C_{11}H_{20}O_2N_2$. Calculated %: N 13.21.

Synthesis of β-(N-Carbethoxyamino)-capric Acid

0.5 g of an ethyl ether solution of chlorocarbonic acid was added dropwise, with cooling, to 1 g of β-aminocapric acid in 10% sodium hydroxide solution (0.67 g) at 0°. The solution was allowed to stand for 1 hour at room temperature, and then, with cooling, was acidified with HCl to Congo red. A white, crystalline precipitate resulted in the amount of 0.79 g (52.1%), m.p. 69-70°.

Found %: C 59.92, 60.01; H 9.53, 9.43; N 5.99, 5.80. $C_{13}H_{25}O_4N$. Calculated %: C 60.23; H 9.65; N 5.41.

Synthesis of the Amide. 0.62 g of the carboethoxy derivative was heated to 40° with 0.28 g (theoretical amount) of thionyl chloride to the cessation of gas bubble evolution. The resulting orange oil was dissolved in 100 ml of dry ether, cooled to −10°, saturated with NH_3, and left to stand overnight. The amide was filtered off, washed with 5% KOH, then with water, and dried. Weight of resulting amide was 0.26 g (43%). After distilling off the ether solution, 0.2 g of non-crystallizing oil resulted. After recrystallization from methyl alcohol with several drops of water added, the resulting amide melted at 152-152.5°. Fine colorless needles.

Found %: C 60.24, 60.31; H 10.20, 10.28; N 10.64, 10.78. $C_{13}H_{26}O_3N_2$. Calculated %: C 60.46; H 10.07; N 10.85.

Synthesis of β-Ureidocapric Acid and 4-Heptyldihydrouracil from β-(N-Carbethoxyamino)capric Acid Amide

0.4 g of the amide was heated on a wire gauze for 1.5 hours with 20 ml of 5% NaOH. The product was cooled to −5° and acidified to Congo red with HCl. There resulted a white, crystalline precipitate of the ureido acid. 0.16 g with m.p. 126-128° was obtained. A sample mixed with the ureido acid isolated previously (m.p. 129-130°) melted at 126-128°.

Found %: C 57.22, 57.27; H 9.61, 9.70; N 11.65, 11.50. $C_{11}H_{22}O_3N_2$. Calculated %: C 57.39; H 9.56; N 12.17.

Synthesis of 4-Heptyldihydrouracil

0.15 g of ureido acid was converted into dihydrouracil under the conditions described above. Crystals with m.p. 181-182° resulted. A sample mixed with dihydrouracil isolated earlier also melted at 181-182°.

Found %: N 13.26. $C_{11}H_{20}O_2N_2$. Calculated %: N 13.21.

Synthesis of β-(N-Benzoylamino)-capric Acid

0.9 g of benzoyl chloride was added dropwise to a solution of 1 g of β-aminocapric acid in 10 ml of 12 N KOH, with cooling to 0°. Following addition of the total amount, stirring was carried on for 1 hour, and then the solution extracted with ether to remove benzoyl chloride excess, cooled, and acidified with HCl to Congo red. A white voluminous precipitate resulted. To remove benzoic acid, it was boiled three times with 50 ml of water, filtered, and dried at 100°. 1.1 g (75.4%), with m.p. 133-134°, resulted. The benzoyl derivative is practically insoluble in hot water; it can be recrystallized from 50% alcohol. It precipitates in the form of very fine needles.

Found %: C 70.04, 69.88; H 8.54, 8.69; N 4.95, 5.01. $C_{17}H_{25}O_3N$. Calculated %: C 70.10; H 8.59; N 4.81.

Synthesis of the Amide. 7.6 g of the benzoyl derivative was heated to 40° with 3.08 g of thionyl chloride to cessation of bubble evolution (about 3 hours). 800 ml of dry ether was put in the flask, the solution cooled to −10°, and saturated with NH_3. The precipitate was filtered off after 12 hours, dried and washed with 5% KOH and water, and then dried again. 7.1 g of amide resulted (93.5%). Upon recrystallization from 70 ml of ethyl alcohol, there resulted 5 g with m.p. 183-184°, and from the mother liquor, 1.9 g with m.p. 163-175°. Colorless needles.

Found %: C 70.08, 70.00; H 9.13, 9.05; N 9.99, 9.89. $C_{17}H_{26}O_2N_2$. Calculated %: C 70.34; H 8.96; N 9.66.

Synthesis of 2-Phenyl-4-heptyl-6-hydroxytetrahydropyrimidine

1.7 g of benzoyl derivative was heated with 2.07 g of thionyl chloride to 80-85°, until bubble evolution ceased. The thionyl chloride excess was distilled off in vacuo and the residue dissolved in 200 ml of absolute ether and saturated with NH_3. No precipitate was obtained. After 12 hours, the ether solution was distilled to one-third of the initial volume and cooled. The resulting precipitate was filtered off and recrystallized from dilute alcohol. The resulting substance melted at 170°. A sample mixed with amide (m.p. 183-184°) melted at 178-180°. Upon further distillation of ether, a non-crystallizing oil resulted. Upon treatment (with heat) with petroleum ether, a portion went into the ether solution. Upon cooling there precipitated from the ether a white crystalline precipitate (long thin needles), m.p. 87-89°. Upon recrystallization from dilute alcohol, the melting point did not change.

Found %: N 10.10, 9.94. $C_{17}H_{24}ON_2$. Calculated %: N 10.29.

A Hofmann Reaction with the Amide of the Benzoyl Derivative of β-Aminocapric Acid

5 g of amide pre-cooled to −10° was added in small portions, with stirring, over a period of 5 hours, to a solution of potassium hypobromite (obtained from 2.5 ml of Br_2 and 9.5 g of KOH in 45 ml of water). After dissolution of the amide, the yellow transparent solution was stirred for another hour and the flask then heated on a water bath to 55° Heating was terminated and the temperature rose spontaneously to 60°. At this time, there was observed discoloration and turbidity of the solution, and the formation of a precipitate. The reaction mass was again heated to 65°, and then immersed in a cooling mixture. The resulting slightly colored oil (II) was separated and the alkaline solution (I) extracted three times with ether. The oil (II) was treated with the same ether. Upon dissolution in ether, there resulted 0.65 g of voluminous precipitate (III). The ether solution was washed several times with HCl (1: 2) (IV).

Isolation of 4-Heptylglyoxalidone Hydrochloride (IV). The acid solution (IV) was extracted with ether and with efficient cooling (ice-salt) was made alkaline with solid KOH. A small amount of crystals resulted. They were extracted with ether and the ether distilled off. 0.22 g of white crystalline material resulted. After recrystallization from a mixture of ethyl ether and petroleum ether, m.p. was 111-112°. A sample mixed with 1-benzoyl-4-heptylglyoxalidone (m.p. 105-106°) melted at 78-82°.

Found %: C 65.03, 65.13; H 11.01, 10.85; N 15.29, 15.39. $C_{10}H_{20}ON_2$. Calculated %: C 65.21; H 10.86; N 15.21.

Isolation of 1-N-Benzoyl-5-heptylglyoxalidone. The ether solution (II) after washing with hydrochloric acid was then washed with 5% KOH solution, followed by water and then distilled. There resulted after recrystallization from petroleum ether, 2.22 g of 1-N-benzoyl-5-heptylglyoxalidone, m.p. 105-106°. Colorless thin needles. A sample mixed with heptylglyoxalidone (m.p. 111-112°) melted at 79-82°.

Found %: C 70.41, 70.30; H 8.45, 8.57; N 9.65, 9.57. $C_{17}H_{24}O_2N_2$. Calculated %: C 70.83; H 8.33; N 9.72.

Investigation of the Alkaline Solution (I). A small precipitate resulted from the alkaline solution of hypobromite (I) upon acidification with HCl (to which had been added beforehand several drops of sodium bisulfite); it was extracted with ether and the ether distilled off. There resulted 0.34 g of acid with m.p. 118-120° A sample mixed with benzoic acid melted at 120-122°.

Investigation of the Precipitate (III). The precipitate resulting from dissolution of oil in ether was washed several times by boiling with alkali and water. Upon acidification of the alkaline wash water, there resulted an acid with m.p. 114-116°, insoluble in hot water, poorly so in ether, readily in alkali and alcohol. With repeated dissolution in alkali and precipitation with acid, the m.p. increased to 128-129° A sample mixed with the benzoyl derivative of β-aminocapric acid (m.p. 133-134°) melted at 130-131°.

The residue washed out from the benzoyl derivative was washed with HCl and water, and then recrystallized 3 times from alcohol. Fine, thin colorless needles resulted with m.p. 216°.

Found %: C 69.62, 69.75; H 8.65, 8.78; N 9.78, 9.95. $C_{34}H_{50}O_4N_4$. Calculated %: C 70.59; H 8.65; N 9.68.

Saponification of 1-N-Benzoyl-5-heptylglyoxalidone. 0.5 g of benzoylglyoxalidone (m.p. 105-106°) was heated with stirring on a boiling water bath with 7 ml of 20% KOH for 5 hours. The flask contents were extracted with ether and the ether solution treated several times with HCl (1: 2). The cooled (ice and salt) acid solution was alkalized with solid KOH and the heptylglyoxalidone extracted with ether. After distillation of the ether, there resulted 0.05 g of colorless needles, m.p. 110-112°. A sample mixed with heptylglyoxalidone, separated earlier (m.p. 111-112°), melted at the same temperature and with benzoylglyoxalidone, at 78-95°. The alkaline mother liquor was acidified with HCl and extracted with ether. After distillation of the ether, there resulted an acid with m.p. 118-121°. A sample mixed with benzoic acid melted at 121-122°.

SUMMARY

1. Synthesis of β-aminocapric acid by interaction of N-octanal with malonic acid in the presence of ammonia has been carried out; the resulting β-amino acid has been characterized by preparation of the following acyl derivatives: urethane, N-benzoyl, and the amides.

2. Synthesis of β-ureidocapric acid has been carried out in two ways: 1) by reacting the β-amino acid with potassium cyanate, and 2) by treating the amide of N-carbethoxy-β-aminocapric acid with dilute alkali. The ureido acid has been converted to the 4-heptyldihydrouracyl derivative in the usual manner.

3. Using a standard method developed in the authors' laboratory, 2-phenyl-4-heptyl-6-dihydroxytetrahydropyrimidine has been prepared from N-benzoyl-β-aminocapric acid.

4. As an example of the Hofmann reaction, carried out with N-benzoyl-β-aminocapric acid amide, reaffirmation has been made of a scheme for intramolecular isomerization of the isocyanic ester, resulting in the formation of the corresponding 1-N-benzoyl-5-heptylglyoxalidone.

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SOLUBILITIES OF SOME β-AMINO ACIDS

V. V. Monblanova and V. M. Rodinov

Interest in β-amino acids has increased markedly over the past decade. It has been found that certain β-amino acids enter into the composition of vitamins and antibiotics, but,at the same time, there do not exist in the literature, papers on research into the physico-chemical properties of these compounds. β-Alanine has attracted most attention on the part of investigators; its solubility in water and in water-alcoholic solutions [1] has been determined, as well as its acid and alkaline dissocation constants [2,3].

A task of the present work has been a quantitative study of the solubility of the β-amino acids in water in relation to their molecular structures, and the effect of hydrogen ion concentration upon the solubility of poorly-soluble acids. β-Phenylalanine, β-(α-naphthyl)-β-alanine and N-methyl-β-phenylalanine were taken as objects of investigation. All of these compounds were obtained according to the method of Rodinov [4, 5, 6].

EXPERIMENTAL

β-Phenylalanine [4] was recrystallized twice from water, m.p. 213-214°; β-(α-naphthyl)-β-alanine [5] was washed with ether, m.p. 214-215°; N-methyl-β-phenylalanine [6] was recrystallized from alcohol, m.p. 169°.

Solubility was determined by the gravimetric method. Amino acid excess was treated with water, or with the investigated solution in the flask which was placed in a thermostat at 25 ± 0.1°. The flask was shaken in a special apparatus until equilibrium was reached. Stirring time was determined individually for each amino acid, for which purpose one sample was preheated to 50° and placed in the thermostat, a second sample being placed immediately in the thermostat. Solubility was in good agreement provided shaking was maintained for not less than 35 hours.

Separation of saturated solution from the precipitate was carried out in the thermostat. A pipette was lowered into the flask, on the lower end of which was threaded a funnel into which was sealed a glass filter. The solution was sucked into the pipette and at the same time was filtered. The resulting filtrate was divided into two parts — in one was determined the amino acid concentration, and in the other concentration of hydrogen ions. The sample in which amino acid concentration was determined was weighed in a weighing tube, dried in the oven at 70-90°, and weighed again. Solubility was determined several times in both water and in various hydrogen ion concentrations.

Hydrogen ion concentration was determined by means of a hydrogen electrode. A saturated calomel electrode was used as the reference electrode. The saturated calomel electrode potential was verified before measurement by standarization against the hydrogen electrode immersed in standard acetate buffer solution at pH 4.62.

β-Amino acid solubilities in water at 25° were determined as given in Table 1. Solubility of β-alanine was taken from the literature [1].

TABLE 1

Solubility of β-Amino Acids in Water at 25°

β-Amino acid	Density	Solubility		Number of measurements
		g/100 g of solution	moles/liter	
β-Alanine	1.1581	—	6.125	
β-Phenylalanine	1	1.982	0.1200	5
β-(α-Naphthyl)-β-alanine	1	0.553	0.00226	8
N-Methyl-β-alanine	1.0636	29.625	1.759	3

The resulting data indicate that the carbon chain structure has the greatest effect upon solubility of the β-amino acids. Introduction of a phenyl group into the chain decreases solubility; the solubility of β-phenylalanine is 51-fold less than the solubility of β-alanine. Introduction of the naphthyl radical produces an even greater decrease in solubility. The solubility of α-(α-naphthyl)-β-alanine is 2710-fold less than the solubility of β-alanine. Introduction of an alkyl radical into the amino group has an opposite effect. The solubility of N-methyl-β-phenylalanine is greater than the solubility of β-phenylalanine by 14.6-fold.

The effect of hydrogen ion concentration upon solubility was investigated, using β-(α-naphthyl)-β-alanine as an example. Solutions with various hydrogen ion concentrations were obtained from chemically-pure HCl, with which the amino acid gives a soluble salt.

TABLE 2

Relationship of β-(α-Naphthyl)-β-alanine Solubility to Hydrogen Ion Concentration

Concentration (moles/liter · 10^2)	pH of initial HCl solution	Solubility (S) moles/liter · 10^2)	pH of the saturated solution
0.87	2.06	0.86	2.69
1.269	1.89	1.244	2.47
2.231	1.65	1.518	2.07
4.31	1.37	2.49	1.71
16.10	1.22	2.956	1.49

Dry residue from hydrochloric acid solution was in the form of amino acid hydrochloride. Calculation was made for free amino acid. The experimental results are given in Table 2 and in the Figure.

It can be seen from the data obtained that solubility increases with increase in hydrogen ion concentration. However, there was not observed a simple relation between these values as occurs with some poorly-soluble α-amino acids [7, 8].

It was not possible to determine the solubility of β-(α-naphthyl)-β-alanine in alkaline solutions, since colloidal solutions were formed, difficult to filter, when the pH exceeded 8.

From the pH values for an equimolecular hydrochloride solution of β-(α-naphthyl)-β-alanine and its solubility, it is possible to determine one of its dissociation constants. The resulting constant will express the alkaline dissocation of the NH_2^- group, provided it be assumed that the neutral form of β-amino acid consists of undissociated molecules. If, however, the neutral form of the amino acid is a bipolar ion, then the constant found will characterize the acid properties of the $CO\bar{O}$ group [9]. At present it can be considered to be proved that an aliphatic amino acid exists in aqueous solution in the form of amphoteric ions.

The β-amino acid investigated by the authors was an aliphato-aromatic acid with an amino group in the aliphatic radical. This made it possible to assume that the neutral form in solution is the bipolar ion, similar to amino acids of the aliphatic series. Under this condition, equilibrium in acid solutions of β-(α-naphthyl)-β-alanine hydrochloride can be expressed by the equation:

$$\overset{+}{NH_3} RCOOH \rightleftharpoons \overset{+}{NH_3} RCO\bar{O} + \overset{+}{H},$$

and the dissociation constant by the following ratio:

$$K = \frac{a_{H+} a_{R\pm}}{a_{R+}}, \qquad (1)$$

where a̲ denotes activity of the corresponding ions.

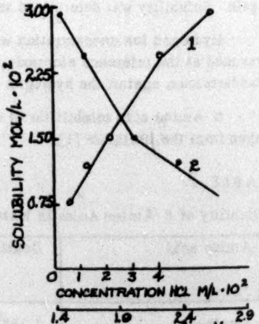
TABLE 3

Approximate Acid Dissociation Constant for β-(α-Naphthyl)-β-alanine

Amino acid concentration (moles/liter)	HCl concentration (moles/liter)	pH of the saturated solution	pK
0.00866	0.00870	2.69	3.21
0.01242	0.01269	2.47	2.94
0.0223	0.01386	2.07	3.07
0.04312	0.0249	1.71	2.98
0.06100	0.02956	1.49	2.99

Since the ionizing power of the solutions investigated by the authors is small, it can be considered, therefore, that the ionic activities are equal to their concentrations. Substituting ionic concentration for ionic activity, and introducing the pH value into equation (1), we have:

$$pK = pH - \log \frac{C_{R\pm}}{C_{R+}}. \qquad (2)$$



Effect of HCl concentration upon the solubility of β-(α-naphthyl)-β-alanine and the relationship of solubility to pH of the saturated solution.

The values $C_{R\pm}$ and C_{R+} can be readily determined from the following ratios:

$$C_{HCl} = C_{Cl'} = C_{R+} + C_{H+},$$

$$C_{R+} = C_{Cl'} - C_{H+}.$$

The total amino acid concentration is known from the solubility (S) value at a given pH value. Hence, the concentration of undissociated molecules is equal to $C_{R\pm} = S - C_{R+}$. Substituting the calculated values of $C_{R\pm}$ and C_{R+} into equation (2), there is obtained the pK value. The results are given in Table 3.

As can be seen from the data obtained (Table 3), the pK value deviates sharply for solutions with low hydrochloric acid concentration where salt hydrolysis may be present, but for the other solutions deviations from the average value constitute only about 3%.

SUMMARY

1. The solubilities of β-phenylalanine, β-(α-naphthyl)-β-alanine and N-methyl-β-phenylalanine in water at 25° have been determined.

2. It has been established that introduction of an aromatic radical into the chain lowers the solubility and that introduction of an alkyl radical into the amino group increases the solubility of β-amino acids.

3. The solubility of β-(α-naphthyl)-β-alanine in solutions with varied hydrogen ion concentrations has been determined.

4. The approximate acid dissociation constant for β-(α-naphthyl)-β-alanine has been calculated.

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* See Consultants Bureau Translation, page 1025.

[illegible] concentration is known then the solubility (S) value at a given pH value. [illegible] of undissociated [illegible] is equal to [illegible]. Substituting the calculated values [illegible] equation (3), [illegible] the pK value. The results are given in Table 4.

As can be seen from the data obtained (Table 3), the pK value [illegible] for solutions with [illegible] acid concentration where salt exchange may be present and for the [illegible] from the [illegible] only [illegible].

SUMMARY

1. The solubilities of [illegible] have been determined.

2. It has been established that introduction of an aromatic radical into the chain lowers the solubility and that introduction of [illegible] increases the solubility of [illegible].

3. The solubility of [illegible] in solutions with varied [illegible] has been [illegible].

4. The [illegible] has been calculated.

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ORIENTATION OF THE TERTIARY-BUTYL GROUP UPON ITS INTRODUCTION INTO THE AROMATIC RING

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It is known that upon the alkylation of aromatic compounds, the position of alkyl groups entering the ring depends upon the nature of the catalyst used. This generally accepted opinion has been confirmed by the authors' works on introduction of the isopropyl group into cumene. It has been demonstrated that when cumene is alkylated by isopropyl alcohol, the position which the entering alkyl radical takes in the aromatic ring varies, depending upon whether $AlCl_3$ or H_2SO_4 is used [1].

On the other hand an interesting variance from this fact is the butylation reaction of m-xylene. Baur [2], who alkylated m-xylene with isobutyl bromide in the presence of $AlCl_3$, and Noelting [3], who carried out this reaction by reacting isobutyl alcohol with m-xylene in the presence of H_2SO_4, both obtained the same product, namely 1,3-dimethyl-5-tertiary-butylbenzene. It was further demonstrated that the same compound is formed also when using such catalysts as $FeCl_3$, BF_3, and others, in the butylation reaction of m-xylene.

It is of interest to note that similar orientation takes place for the tertiary-butyl group when the secondary-butyl group is introduced into m-xylene in the presence of H_2SO_4, as well as BF_3, forming the 1,3,4-isomer [4].

This fact gives reason for assuming that there is also shown a strong effect by the nature (structure) of the entering alkyl group itself upon orientation of the alkyl group into the benzene ring.

An isomeric hydrocarbon, with substituent positions of 1,3,4, was obtained in the pure state from the organomagnesium compound derived from 1,3-dimethyl-4-iodobenzene and tertiary-butyl chloride [5]. It was shown that 1,3-dimethyl-4-tertiary-butylbenzene reacted with $AlCl_3$ and rearranged into symmetrical dimethyl-tertiary-butylbenzene.

Constants for the isomeric butyl-m-xylenes obtained by various methods are given in Table 1.

TABLE 1

Butyl-m-xylene obtained	Constants			Oxidation products	Literature
	Boiling point (in °)	n_D^{37}	d^{37}		
According to the Grignard reaction	210-214	1.5030	0.9372	Trimellitic acid (1,2,4)	[5]
By butylation of m-xylene with tertiary-butyl chloride in the presence of $AlCl_3$	200-202	1.4890	0.8619	Trimesinic acid (1,3,5)	[5]
By heating the hydrocarbon, obtained according to Grignard, with $AlCl_3$	202-203	1.4903	0.8720	The same	[5]
By butylation of m-xylene with isobutyl alcohol in the presence of H_2SO_4	200-204	–	–	–	[3]
By butylation of m-xylene with isobutylene in the presence of $AlCl_3$	204-206	n_D^{15} 1.4980	d^{15} 0.870	–	[6]

In a work by I. K. Sivkov and coworkers published recently [7], are found brief directions for forming 1,3,5-tertiary-butyl-m-xylene as well as the 1,3,4-isomer from the m-xylene butylation reaction in the presence of H_2SO_4; the effect of H_2SO_4 concentration upon yield of unsymmetrical isomer is noticeable.

However, in none of the cases was the amount of 1,3,4-isomer formed given. Moreover, there was no convincing proof given of the presence of unsymmetrical isomers.

Since the above point is of considerable interest, the authors undertook experimental work for the purpose of clarifying whether or not there is formed any considerable amount of 1,3,4-dimethyl-tertiary-butylbenzene during the butylation reaction of m-xylene with H_2SO_4 present.

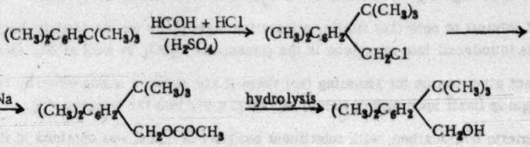
The authors' experiments on butylation of m-xylene with isobutyl alcohol in the presence of H_2SO_4 led to synthesis of 1,3-dimethyl-5-tertiary-butylbenzene, yield of which consitituted about 40% of theory, calculated on the basis of m-xylene entering into reaction, or about 20%, based upon m-xylene taken for reaction (see Table 2 for constants). The unsymmetrical isomer, even if it is formed (which the authors did not prove), is in considerably smaller amount, and can by no means be considered as one of main reaction products.

TABLE 2

Butyl-m-xylene obtained by alkylation of m-xylene in the presence of H_2SO_4	Constants			Melting point (in °)	
	B. p. (in °)	n_D^{20}	d_4^{20}	Trinitro derivative	Corresponding benzyl alcohol
Before heating with $AlCl_3$	204-204.5	1.4962	0.8656	111-112*	98-99**
After heating with $AlCl_3$	203-205	1.4960	0.8665	111-112*	98-99**

The authors did not observe conversion into another isomer upon heating the product obtained by butylation with $AlCl_3$.

Identity of the tertiary-butyl-m-xylene before and after heating with $AlCl_3$ was demonstrated by the authors in preparing the trinitro derivatives and the corresponding trialkyl substituted benzyl alcohols. The latter were prepared according to the scheme:



$$(CH_3)_2C_6H_3C(CH_3)_3 \xrightarrow[(H_2SO_4)]{HCOH + HCl} (CH_3)_2C_6H_2\left\langle\begin{matrix}C(CH_3)_3\\ CH_2Cl\end{matrix}\right. \longrightarrow$$

$$\xrightarrow[pyridine]{CH\ COONa} (CH_3)_2C_6H_2\left\langle\begin{matrix}C(CH_3)_3\\ CH_2OCOCH_3\end{matrix}\right. \xrightarrow{hydrolysis} (CH_3)_2C_6H_2\left\langle\begin{matrix}C(CH_3)_3\\ CH_2OH\end{matrix}\right.$$

Constants for the initial hydrocarbons and the hydrocarbons resulting after heating with $AlCl_3$, as well as the constants for these hydrocarbon derivatives, are given in Table 2.

These data indicate that dimethyl-tertiary-butylbenzene obtained by butylation of m-xylene with isobutyl alcohol in the presence of H_2SO_4 does not isomerize upon heating with $AlCl_3$.

Having demonstrated experimentally literature claims to the fact that in the butylation reaction of m-xylene there occurs preferentially formation of dimethyl-tertiary-butylbenzene of symmetrical structure, regardless of the character of the condensing agent used (H_2SO_4 or $AlCl_3$), it appeared of interest to the authors to clarify whether or not it is a general mechanism characteristic for introduction of the tertiary-butyl group into an aromatic hydrocarbon molecule. Certain data on this problem can be found in recently published literature [8] where it is pointed out that introduction of the tertiary-butyl group into the isopropylbenzene molecule in the presence of H_2SO_4 and $FeCl_3$ leads to formation of 1,4-isopropyl-tertiary-butylbenzene as the principal reaction product (0.9 of the total yield), at the same time that introduction of the isopropyl group into the tertiary-butylbenzene under the same conditions forms m- and p-isomers in approximately equal amounts. The authors decided to examine this fact, using as an illustration of butylation, the simplest aromatic hydrocarbon—benzene.

With regard to the structure of dialkyl derivatives which are formed upon butylation of benzene in the presence of $AlCl_3$, there can be found contradictory data in the literature. Introduction of two tertiary-butyl groups into benzene was realized back in the last century by butylation of benzene, both in the presence of $AlCl_3$ [9] and in the presence of H_2SO_4 [10]. In both instances the resulting hydrocarbon was that in which the tertiary butyl groups were found to be in the p-position. Later on, di-tertiarybutylbenzene was synthesized repeatedly by various chemists, via the butylation of benzene in the presence of various catalysts ($AlCl_3$, H_2SO_4, BF_3, HF, $FeCl_3$, P_2O_5, HCl).

There was observed in all cases formation of the p-isomer, with m.p. 76-78°. Only in 1947 did there appear a patent [11] in which, for the first time, there was indicated formation of the m-isomer along with p-di-tertiary-butylbenzene by the alkylation of benzene with isobutylene in the presence of $AlCl_3$. It was indicated in the patent that m-di-tertiarybutylbenzene (for its constants see Table 3) can also be obtained by the isomerization of p-di-tertiarybutylbenzene in the presence of $AlCl_3$ with simultaneous passage of hydrogen chloride through the mixture. Other investigators noted later that it was not possible to synthesize m-di-tertiarybutylbenzene by alkylation of benzene with isobutylene. Synthesis of m-di-tertiary-butylbenzene has been realized from 2,4-ditertiarybutylphenol, according to the following equation [12]:

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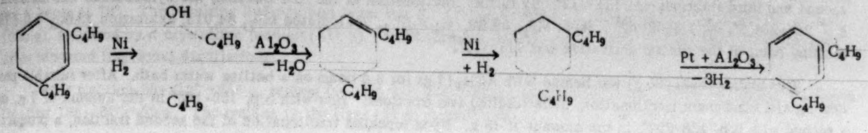
* A mixed sample did not give depression upon melting.

**According to the literature data, m.p. of 1,3-dimethyl-5-tertiary-butyl-benzyl alcohol is 99° [4]. Mixed sample on melting did not give depression.



The constants for m-di-tertiarybutylphenol synthesized in such manner coincide with the constants given for the same hydrocarbon in the patent earlier mentioned (Table 3).

TABLE 3

m-Di-tertiarybutylbenzene synthesized	Constants			
	B. p. (in °)	n_D^{20}	d_4^{20}	M. p. (in °)
By alkylation of benzene with isobutylene in the presence of $AlCl_3$ [11]	78.5 at 4.4 mm	1.4870	–	−10.6
From 2,4-di-tertiarybutylphenol	73 at 2.5 mm	1.4879	0.8589	–

In 1951 data were again published, confirming formation of 1,3-di-tertiarybutylbenzene from the alkylation of benzene with isobutylene in the presence of $AlCl_3$ [13].

The authors' experiments on butylation of benzene led only to formation of p-di-tertiarybutylbenzene. Alkylation of benzene was realized by reaction of benzene with isobutyl alcohol in the presence of H_2SO_4, and also with isobutyl chloride in the presence of $AlCl_3$. In both cases there resulted a hydrocarbon of m.p. 77-78°.

A mixed sample of dialkylbenzenes obtained by butylation of benzene in the presence of these two condensing media did not give depression upon melting. Experiments set up by the authors on rearrangement of p-di-tertiary-butylbenzene in the presence of $AlCl_3$ did not lead to formation of m-ditertiarybutylbenzene. The experiments were carried out under various conditions: temperature and reaction were varied. In addition, experiments were carried out with passage of gaseous hydrogen chloride through the reaction. Thus, the indications to be found in the American patent [11] concerning the isomerization of p-di-tertiary-butylbenzene by heating it with $AlCl_3$ have not been confirmed.

The authors' experiments have indicated that the alkylation of benzene by isobutyl alcohol in the presence of H_2SO_4, and with isobutyl chloride in the presence of $AlCl_3$, as well as by heating p-di-tertiarybutylbenzene with $AlCl_3$, do not result in formation of the m-isomer.

This indicates that introduction of the tertiary butyl group into an aromatic hydrocarbon is evidently characterized by the fact that the position of entry of this group is not dependent to any high degree upon the nature of the condensing agent used (H_2SO_4 or $AlCl_3$). There apparently exists in this case the stronger effect of factors which inhibit the orienting effect of a condensing substance.

TABLE 4

Fraction number	B. p. (in °)	n_D^{20}	Quantity (in g)	M. p. of the trinitro derivative (in °)*
1	201-205	1.4960	42	110-111
2	205-210	1.4961	14	112-113
3	210-214	1.4970	3	111-112

It is of interest to mention that upon introducing a tertiarybutyl group into both benzene and m-xylene, there proceeds the formation of symmetrically-composed molecules – in the first instance, of p-ditertiary-butylbenzene, and in the second, of 1,3-dimethyl-5-tertiary-butylbenzene. This characteristic is perhaps, to some degree, connected with the volume taken up by the highly branched tertiary-butyl group.

EXPERIMENTAL

1. Alkylation of m-Xylene by iso-Butyl Alcohol in the Presence of H_2SO_4

Reaction was carried out by the standard procedure for alkylation of aromatic hydrocarbons with alcohols in the presence of H_2SO_4. 95 g of isobutyl alcohol (b.p. 106-108°) and 278 g of commercial sulfuric acid were taken for 136 g of m-xylene (b.p. 138-139°). After appropriate processing, the reaction product was fractionated at atmospheric pressure. The following fraction resulted from double fractionation (Table 4).

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* A m.p. of 110° [2] and of 113° [14] has been indicated in the literature for the trinitro derivative of 1,3-dimethyl-5-tertiarybutylbenzene.

Mixed samples of the trinitro derivatives, from the first and second fractions, melted at 110.5-111.5°; from the second and third fractions – at 111-112°. By further fractionation of the first fraction, the hydrocarbon was isolated: b.p. 204-204.5°; n_D^{20} 1.4962; d_4^{20} 0.8656; MR_D 54.69. $C_{12}H_{18}F_3$. Calculated MR_D 54.015, exaltation ΣMR_D + 0.675; melting point of the trinitro derivative was 111-112°.

This hydrocarbon (35 g) was heated with $AlCl_3$ (7 g) for 3.5 hours on a boiling water bath. After suitable processing and subsequent fractionation, there resulted two fractions: first with b.p. 150-198° in the amount of 7 g, and a second with b.p. 198-207°, in the amount of 18 g. Upon repeated fractionation of the second fraction, a product was isolated (14.5 g) which had:

M.p. 203-205°; n_D^{20} 1.4960; d_4^{20} 0.8665; MR_D 54.61. $C_{12}H_{18}F_3$. Calculated: MR_D 54.015, exaltation ΣMR_D + 0.592; melting point of the trinitro derivative was 111-112°. A sample mixed with the trinitro derivative prepared earlier from the initial hydrocarbon which was not heated with $AlCl_3$, melted at 111-112°.

2. Synthesis of 1,3-Dimethyl-5-tertiary-butylbenzyl Alcohol

50 g of formalin (39.7%) and 79 g of hydrochloric acid (35%) were mixed with 100 g of 1,3-dimethyl-tertiary-butylbenzene (obtained by butylation in the presence of H_2SO_4) and 200 g of commerical hydrochloric acid added at 50° over 1.5 hours. After this, the reaction mass was stirred at 60° for an additional 6 hours. After suitable processing and subsequent vacuum fractionation of the reaction product, there resulted 48 g of fraction containing 98.5% of chloromethyl derivative, which constituted 36.3% of theoretical yield.

B.p. 118-120° (4 mm); n_D^{20} 1.5300; d_4^{20} 1.0084; MR_D 64.51. $C_{13}H_{19}ClF_3$. Calculated: MR_D 63.50, exaltation ΣMR_D + 1.01.

In addition, there resulted a crystalline product (24 g) of m.p. 134-135°, corresponding to the hydrocarbon di-(2,6-dimethyl-4-tertiary-butylphenyl)methane [15].

Found %: C 89.44, 89.67; H 10.83, 10.83; $C_{25}H_{36}$. Calculated %: C 89.28; H 10.72.

By chloromethylation of dimethyl-tertiary-butylbenzene (30 g) isolated from the hydrocarbon that was heated with $AlCl_3$, there was obtained 17 g of a fraction containing 99.9% of the chloromethyl derivative, which constituted 43.6% of theoretical yield: b.p. 136-137° (11 mm), n_D^{20} 1.5296.

Conversion of the chloromethyl derivative into the corresponding acetoxy derivative was realized in the following manner: 39 g of 1,3-dimethyl-5-tertiary-butyl-benzyl chloride (obtained from the hydrocarbon that was not heated with $AlCl_3$), 25 g of anhydrous sodium acetate and 0.5 g of pyridine were placed into a round-bottomed flask equipped with stirrer, thermometer and reflux condenser. The mixture was heated in such a manner that the temperature would reach 80° during the first hour, and during the next 2 hours would reach 125°. The reaction mass was stirred at this temperature for 4 hours, and then was cooled to 80°; 40-50 g of water was added, and it was stirred again for 30 minutes at 80°. After washing and drying over $CaCl_2$, the reaction product was fractionated in vacuo. The product isolated was in the amount of 29 g, which contained 98.4% of ester, calculating on the basis of 1,3-dimethyl-tertiary-butylbenzyl acetate. The yield of acetate amounted to 67% of theory. The acetate obtained possessed the following constants:*

B.p. 127-129° (2 mm), n_D^{20} 1.5059, d_4^{20} 0.9835, MR_D 70.67. Calculated: MR_D 69.52, exaltation ΣMR_D + 1.15.

Found %: C 77.21, 77.00; H 9.50, 9.36. $C_{15}H_{22}O$. Calculated %: C 76.92; H 9.40.

1,3-Dimethyl-5-tertiary-butylbenzyl acetate was synthesized in similar fashion from the chloromethyl derivative prepared from the hydrocarbon heated with $AlCl_3$. The product contained 98% of the acetate.

The boiling point of the resulting acetate was 151-152° (10 mm), n_D^{20} 1.5064.

Both acetates obtained by saponification with 10% alcoholic NaOH solution gave the same dimethyl-tertiary-butylbenzylic alcohol, with m.p. 98-99° [4]. A sample of the two alcohols when mixed melted at the same temperature.

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* There is described in the literature the synthesis of 2,4-dimethyl-6-tertiary-butyl-benzyl acetate by the interaction of dimethyl-tertiary-butylbenzyl chloride, acetic anhydride and acetic acid in the presence of CH_3COOK. However, the constants of the resulting acetate are not given [4].

Found %: C 81.21, 81.23; H 10.66, 10.75. $C_{13}H_{20}O$. Calculated %: C 81.24; H 10.41.

3. Alkylation of Benzene with Isobutyl Alcohol in the Presence of H_2SO_4

1400 g of commercial sulfuric acid was added with stirring to a mixture consisting of 550 g of benzene and 250 g of isobutyl alcohol (b.p. 106-108°) over a period of 1 hour at 60°. Stirring of the mixture was then continued for 6 hours at 70°. The resulting hydrocarbon layer was distilled with steam, a liquid portion distilling off at first (530 g), followed by a crystalline product (115 g). The following fractions were isolated from the liquid portion after repeated fractional distillations:

First fraction 80-110° – 244 g, second fraction 110-166° – 23 g, third fraction, 166-168° – 121 g, and the fourth fraction 168-180° – 53 g. The residue in the flask (20 g) crystallized.

The third fraction had: n_D^{20} 1.4911; d_4^{20} 0.8636, MR_D 44.94. $C_{10}H_{14}\digamma_3$. Calculated: MR_D 44.76.

These constants correspond to literature data for tertiary-butylbenzene [16]. The yield of tertiary-butylbenzene amounted to 31-32% of theory, calculating on the basis of benzene entering into reaction. The crystalline product, recrystallized from ethyl alcohol, had a m.p. of 77-78°, corresponding to di-tertiary-butylbenzene.

Found %: C 88.43, 88.77; H 11.39, 11.61. $C_{14}H_{22}$. Calculated %: C 88.42; H 11.58.

The yield of p-di-tertiary-butylbenzene amounted to 24-25% of theory, calculating on the basis of benzene entering into reaction.

4. Alkylation of Benzene with Isobutylchloride in the Presence of $AlCl_3$

Reaction was carried out under the usual conditions of aromatic hydrocarbon alkylation by alkyl halides in the presence of $AlCl_3$. 20 g of benzene, 16 g of isobutyl chloride (b.p. 67-70°) and 3 g of $AlCl_3$ were taken for reaction. On fractionation of the reaction product (after suitable processing) the following fractions resulted: first fraction 70-100° – 5 g; second fraction 160-210° – 8 g; and third fraction 210-236° – 10 g. By a second distillation of the second fraction, there were isolated from the latter tertiary-butyl benzene (b.p. 166-168°) and a fraction of b.p. 210-220°, from the latter of which, upon cooling, crystallized out a product of m.p. 75-76°.

Similar crystalline products were also isolated by freezing out from the 210-236° b.p. fraction (third fraction). After recrystallization from alcohol, m.p. was 77-78°. A sample mixed with p-di-tertiary-butylbenzene obtained from alkylation of benzene with isobutyl alcohol in the presence of H_2SO_4, melted at the same temperature.

p-Di-tertiary-butyl benzene was heated with $AlCl_3$. The experiments were carried out under various conditions: by heating the mixture on a boiling water bath for 6 hours, and for 4 hours; by heating the mixture at 70-90° for a period of 2-3 hours with simultaneous passage of gaseous hydrogen chloride into the reaction mixture. It should be pointed out that considerable resinification was observed in all experiments. From the reaction products a small amount of liquid product was separated, distilling over a wide range (5 g from 27 g of hydrocarbon taken for reaction, and in another experiment 1 g from 17 g of initial hydrocarbon). By repeated fractionations of the separate fractions, it was possible to isolate a small amount of product with the following constants:*

B.p. 93-98° (10 mm); n_D^{20} 1.4940; d_4^{20} 0.8688; MR_D 63.66. $C_{14}H_{22}\digamma_3$. Calculated: MR_D 63.25.

This product was found to be non-homogeneous. Upon standing, crystals of p-di-tertiary-butylbenzene with m.p. 76-77° precipitated.

SUMMARY

It has been demonstrated that the wide-spread opinion regarding formation of various isomers by alkylation of aromatic hydrocarbons, depending upon the catalyst used ($AlCl_3$ or H_2SO_4) is not justifiable in the case of the tertiary-butyl group introduction into benzene and m-xylene. In these cases there exists a tendency toward formation of symmetrically-composed molecules: 1,3-dimethyl-5-tertiary-butylbenzene in the case of m-xylene butylation, and 1,4-di-tertiary-butylbenzene in the case of benzene butylation.

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* The constants obtained do not conform to the literature data for m-di-tertiary-butylbenzene [12].

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* See Consultants Bureau Translation, page 299.

THIOCYANOGENATION OF UNSATURATED COMPOUNDS

I. THIOCYANOGENATION OF UNSATURATED HYDROCARBONS AND OF SILICON-HYDROCARBONS

A. A. Bugorkova, L. N. Petrova and V. M. Rodinov

The similarity in properties of free thiocyanogen with those of the halogens has been the basis for use of thiocyanogen as a reagent for quantitative determination of unsaturated compounds. Free thiocyanogen polymerizes very readily; when dissolved in carbon tetrachloride, chloroform, benzene and carbon disulfide and especially in anhydrous acetic acid, it is relatively stable [1].

The thiocyanogen reaction was first used to determine the extent of acetoacetic ester enolization, and then for determining the degrees of unsaturation of the aliphatic oils of castor, olive, peanut, and others.

A study of the addition of thiocyanogen to oleic, linoleic, linolenic, erucic and brassidic acids has indicated that this reaction proceeds normally [2]. Thus, in the case of linoleic acid, thiocyanogen adds to one of the two ethylenic bonds, and in the case of linolenic acid, to two of the three. Because of this fact, the number of equivalents of thiocyanogen that will add to a given acid does not correspond to the number of bromine equivalents added, when used for analysis of fats and oils.

The feasibility of using thiocyanogen numbers along with iodine and bromine numbers for characterization of unsaturated compounds in other areas of organic chemistry has hardly been touched upon (an exception representing abietinic acid [3]). Only one work is known [4] wherein the author quotes certain data concerning the addition or non-addition of thiocyanogen to a number of compounds which enter into the composition of the ester oils, but no attempt was made to generalize or to clarify the results obtained.

In the study of thiocyanogenation, as an investigative method for ester oils and aromatic substances, the authors tried first of all to apply this procedure to terpene hydrocarbons. Up to the present time there have been no accurate chemical methods for determination of bicyclic hydrocarbons containing one double bond (pinene, carene) in the presence of hydrocarbons containing additional double bonds (dipentene, terpinolene).

The bromination reaction is useless for such purpose since the ring is ruptured by addition of bromine, and the resulting bromine number exceeds considerably the calculated.

It was the authors' assumption that thiocyanogen as a less reactive reagent will not give side-reactions, which was confirmed: α-pinene, β-pinene and Δ^3-carene gave thiocyanogen numbers (Table 1) approximating closely the calculated. Side reactions proceed more slowly with thiocyanogenation than with bromination.

Further investigations have demonstrated that reactivity of the double bond containing a tertiary carbon atom is considerably greater than reactivity of primary and secondary double bonds.

TABLE 1

Addition of Thiocyanogen to Unsaturated Hydrocarbons

Hydrocarbon	Character of the double bond	Percent added			
		Bromine	Thiocyanogen		
		within 5 minutes	within 5 minutes	within 1 hour	within 24 hours
α-Pinene	Tertiary-secondary	246.6	99.7	102.8	157.5
β-Pinene	Tertiary-secondary	227.0	99.3	103.7	151.7
Δ^3-Carene	Tertiary-secondary	146.7	97.9	124.8	135.7
Cyclohexane	Secondary-secondary	98.8	12.9	40.0	96.9
Heptene-1	Primary-secondary	97.7	12.4	36.8	55.0
4,4-Dimethylpentene-1	Primary-secondary	99.3	4.1	23.9	49.4

It can be seen from the data of Table 1 that hydrocarbons having double bonds between the primary and secondary carbon atoms add, within 24 hours, approximately 50% of the calculated quantity of thiocyanogen; within the same time period, cyclohexene, with a double bond between secondary carbon atoms, adds thiocyanogen completely, and terpene hydrocarbons with double bonds at tertiary carbon atoms add thiocyanogen completely within 5 minutes.

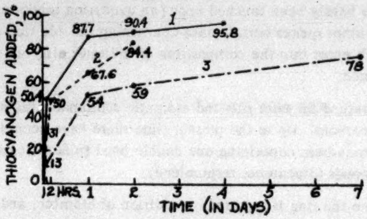
The same pattern was observed by the authors for unsaturated compounds containing functional groups as well.

Results obtained by the authors for bicyclic hydrocarbons gave rise to hope that the thiocyanogen method might offer an opportunity for solving the question of determining them in the presence of hydrocarbons containing two double bonds (for example, limonene in the presence of pinene). It was found, however, that limonene reacts quite rapidly with one molecule of thiocyanogen, and exceptionally slow with the other Complete addition of thiocyanogen to limonene is attained only after 96 hours.

With the example of limonene, there was also studied in greater detail 2,10-dimethyl-dodecadiene, as well as diallyl, and the same phenomenon of predominant addition of thiocyanogen to one of the two bonds of diolefinic compounds was observed, as up to the present time has been observed only with linoleic acid.

In order to solve the problem of whether in actuality the addition of thiocyanogen to one double bond inhibits thiocyanogenation of the second bond, the authors investigated the behavior of diallyl —a hydrocarbon with two identical bonds.

Within the first 25 hours one of the double bonds of diallyl added thiocyanogen completely; however, addition to the second bond proceeded only 56% in 7 days. The diallyl thiocyanogenated product obtained during that period corresponding to addition of one thiocyanogen molecule only, and having, according to the authors' assumption, the structure $CH_2(SCN)CH(SCN)CH_2CH_2CH{=}CH_2$, was a heavy, red-brown liquid, and contained 13.97% N (for $C_8H_{10}S_2N_2$ Calculated %: N 14.1).



Quantity of thiocyanogen added, in % of theory. 1) Limonene; 2) dimethyldodecadiene; 3) diallyl.

The double bond of the substance isolated reacted with bromine very rapidly (similarly to that of diallyl), and added thiocyanogen very slowly.

Upon prolonged thiocyanogenation with a solution of higher concentration, the authors succeeded in isolating diallyl tetrathiocyanogen $CH_2(SCN)CH(SCN)CH_2CH_2CH(SCN)CH_2(SCN)$ — a yellow crystalline compound, m.p. 168° (with decomposition).

By combining data of the authors with data of the literature, a deduction can be made that compounds containing two double bonds add thiocyanogen at one bond with considerably greater rapidity than at the second bond.

In determining unsaturation of organosilicon compounds, the bromination reaction does not always give satisfactory results.

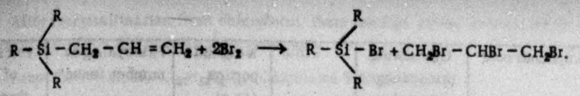
After studying the thiocyanogen addition to double bonds of unsaturated compounds containing silicon, the authors determined that the presence of silicon promotes addition of thiocyanogen, which can be explained on the basis of a higher positive silicon charge.

Silicon hydrocarbons containing a double bond between primary and secondary carbon atoms are considerably more reactive than hydrocarbons of similar structure which do not contain silicon. Particularly clear-cut is the effect of silicon upon addition of thiocyanogen to a double bond in position 2,3. Monoallyl derivatives, as can be seen in Table 2, react almost immediately with the thiocyanogen molecule, although the character of the remaining three radicals bound to silicon also has some effect upon the addition rate.

If two or three allyl groups are present in the silicon hydrocarbon molecule, then their various bonds, in contrast to the olefinic hydrocarbons, will react with thiocyanogen independently of one another. However, the reaction rate decreases somewhat in proportion to the increase in number of allyl groups.

Rearrangement of the double bond in silicon hydrocarbons to positions 3,4 and 4,5 slows down the addition of thiocyanogen somewhat, to that approximating analogous aliphatic hydrocarbons.

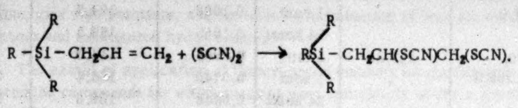
When reacting bromine with unsaturated silicon hydrocarbons, there occurs addition of excessive amounts of bromine (as compared with the calculated), due to rupture of the molecule [5].



$$R-\overset{R}{\underset{R}{Si}}-CH_2-CH=CH_2+2Br_2 \longrightarrow R-\overset{R}{\underset{R}{Si}}-Br+CH_2Br-CHBr-CH_2Br.$$

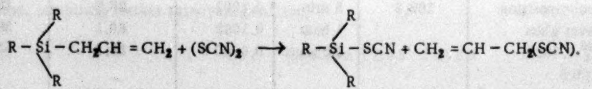
It has been determined by the authors that for thiocyanogenation of each double bond of a silicon hydrocarbon, there is consumed exactly one molecule of thiocyanogen.

The thiocyanogenation reaction can proceed either in the direction of addition at the double bond of thiocyanogen,



$$R-\overset{R}{\underset{R}{Si}}-CH_2CH=CH_2+(SCN)_2 \longrightarrow R\overset{R}{\underset{R}{Si}}-CH_2CH(SCN)CH_2(SCN).$$

or in the direction of rupture of the silicon hydrocarbon without subsequent addition of thiocyanogen at the double bond,



$$R-\overset{R}{\underset{R}{Si}}-CH_2CH=CH_2+(SCN)_2 \longrightarrow R-\overset{R}{\underset{R}{Si}}-SCN+CH_2=CH-CH_2(SCN).$$

In order to illustrate the problem of direction of the reaction, the authors isolated a product resulting on reaction of thiocyanogen with triallylethylsilane. The resulting product was a solid crystalline material containing nitrogen in amount corresponding to the composition $C_{17}H_{20}SiS_6N_6$.

This fact makes it possible to assume that thiocyanogenation of unsaturated silicon hydrocarbons proceeds in the direction of double bond addition.

TABLE 2

Thiocyanogen Addition to Unsaturated Silicon Hydrocarbons

Silicon hydrocarbon	Percent thiocyanogenation within		
	5 minutes	1 hour	24 hours
Trimethylallylsilane	93.3	93.9	–
Triethylallylsilane	96.4	96.4	–
Tripropylallylsilane	92.2	97.3	–
Triethylisobutenylsilane	97.2	99.3	–
Methyldiallylsilane	76.8	93.7	–
Methyltriallylsilane	81.6	95.6	–
Trimethylbutenylsilane	6.9	37.7	99.6
Triethylmethylpentenylsilane	5.2	31.2	93.0
Dimethylphenylmethylpentenylsilane	13.8	24.1	96.2

The unsaturated silicon hydrocarbons were submitted by V. F. Mironov; for their syntheses and properties, see [8].

EXPERIMENTAL

The solution of free thiocyanogen was prepared by action of bromine upon lead thiocyanate in anhydrous acetic acid [6].

The experimental data are given in Table 3, where, in the first column, are enumerated substances used for the investigation, with indications for their methods of synthesis and their properties.

Synthesis of diallyl dithiocyanide. 1 g of diallyl was treated with 250 ml of thiocyanogen solution in glacial acetic acid (1: 6). The acetic acid was neutralized after 24 hours with sodium carbonate to the appearance of an

TABLE 3

Names and properties of the compounds used in the investigation	Calculated thiocyanogen or bromine number	Time	Weighed portion (in g)	Thiocyanogen number found	Percent of theory
a-Pinene: b.p. 20-21° (1 mm); n_D^{20} 1,4660; d_4^{20} 0,8580; bromine number (5 min.) 246.6	117.25	5 min.	0,0940	117.0	99.7
		1 hour	0,1030	120.6	102.8
		24 hours	0,0732	184.8	157.5
β-Pinene: b.p. 161-162°; n_D^{20} 1,4754; d_4^{20} 0,8720; bromine number (5 min.) 227.0	117.25	5 min.	0,1088	116.5	99.3
		1 hour	0,1008	121.7	103.7
		24 hours	0,1055	168.5	143.6
Δ^3-Carene: b.p. 167-169°; n_D^{20} 1.4720; d_4^{20} 0,8640; bromine number (5 min.) 192.3	117.25	5 min.	0,0966	114.3	97.4
		1 hour	0,0740	146.4	124.8
		24 hours	0,0648	159.3	135.8
Cyclohexene: b.p. 83°; n_D^{20} 1.4450; d_4^{20} 0,8198; bromine number 192.3	194.5	5 min.	0,1084	25.2	12.9
		1 hour	0,1141	77.9	40.05
		24 hours	0,1095	188.5	96.9
Heptene-1 was obtained by decomposition of heptyl acetate by passage over glass chips at 475°: b.p. 93-94°; d_4^{20} 0.7020; n_D^{20} 1.4004; bromine number 159.5	162.8	5 min.	0,1001	20.2	12.4
		1 hour	0,1062	60.1	36.8
		24 hours	0,0950	89.8	55.0
4,4-Dimethylpentene-1: b.p. 71-72°; n_D^{20} 1.3925; d_4^{20} 0.6991; bromine number (5 min.) 161.6	162.8	5 min.	0,0744	6.68	4.1
		1 hour	0,0773	38.9	23.9
		24 hours	0,0826	80.5	49.4
Limonene: b.p. 62-63° (12 mm); n_D^{20} 1.4732; d_4^{20} 0,8440; bromine number (5 min.) 236.3	234.6	5 min.	0,1066	71.07	30.3
		1 hour	0,0842	118.2	50.4
		24 hours	0,0707	206.2	87.7
		2 days	0,0802	212.0	90.4
		4 days	0,0809	224.4	95.8
Diallyl was obtained according to the Grignard reaction [7]: b.p. 58-58.2° (744 mm); n_D^{20} 1.4012; d_4^{20} 0.6873; bromine number (5 min.) 389.3	389.2	5 min.	0,0933	0	0
		1 hour	0,0788	51.6	13.3
		24 hours	0,0631	210.2	54.0
		2 days	0,0554	231.05	59.4
		4 days	0,0668	266.35	68.4
		7 days	0,0735	305.1	78.4
2,10-Dimethyldodecadiene: b.p. 239-240°; n_D^{20} 1.4453; d_4^{20} 0.7930; bromine number (5 min.) 159.2	164.5	5 min.	0,0987	9.7	5.9
		1 hour	0,1015	51.2	31.1
		2 hours	0,0980	82.3	50.0
		24 hours	0,0926	113.5	67.6
		2 days	0,0924	139.4	84.4

oily layer. The oil was extracted with ether. After removal of ether from the ether extract, which was dried beforehand over calcium chloride, a red-brown oil remained, possessing an unpleasant odor, readily soluble in alcohol. The product was purified to remove resins by boiling with carbon. After removal of the alcohol, a dark-yellow oil remained.

Found %: N 13.97. $C_8H_{10}S_2N_2$. Calculated %: N 14.12.

Thiocyanogen number. Found: After 24 hours, 43.0; after 48 hours, 61.76. Calculated as diallyl dithiocyanide: 80.8

Synthesis of a completely thiocyanogenated diallyl product. 570 ml of 0.2 N thiocyanogen solution in glacial acetic acid (1: 15) was added to 1 g of diallyl. The reaction mixture was left for one week. After completion of reaction, there settled out to the bottom a precipitate of yellow flakes which dissolved upon shaking the flakes and passing through a filter. The solution was neutralized to a weakly acid reaction and the precipitate was filtered off. The reaction product was in the form of a yellow precipitate, insoluble in water, alcohol, ethyl acetate, acetic acid, and poorly soluble in chloroform.

After recrystallization from chloroform, there resulted yellow crystals which melted at 167-169° (with decomposition), which did not add thiocyanogen.

Found %: N 17.38. $C_{10}H_{10}S_4N_4$. Calculated %: N 17.8

SUMMARY

1. The thiocyanogen addition reaction differs greatly from the addition reaction of halogens, first of all in its selectivity.

2. Thiocyanogenation permits determination of double bonds in those compounds which, under the action of bromine, give side reactions, and for which determination of bromine numbers is impossible (bicyclic terpene hydrocarbons and unsaturated hydrocarbons).

3. The extent of application of thiocyanogen numbers for quantitative determination purposes is limited to the unsaturated compounds for which reaction goes completely within a practical time period – not more than 24 hours. The thiocyanogen reaction is not suitable for determination of hydrocarbons containing primary-secondary double bonds.

4. In the case of limonene, diallyl and dimethyldodecadiene, addition of thiocyanogen proceeds at one double bond, inhibiting further thiocyanogenation.

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All-Union Research Institute
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Substances

THIOCYANOGENATION OF UNSATURATED COMPOUNDS

II. EFFECT OF OXYGEN-CONTAINING FUNCTIONAL GROUPS UPON THE THIOCYANOGENATION REACTION

A. A. Bugorkova, L. N. Petrova and V. M. Rodionov

The presence of oxygen-containing functional groups modifies considerably reactivity of the double bond. It has been determined by the authors that the presence, near the double bond, of carbinol, as well as of the carbonyl and carboxyl groups, inhibits the thiocyanogenation reaction.

Data are given in Table 1 for thiocyanogenation of unsaturated alcohols, aldehydes, ketones, carboxylic acids and their derivatives, with differently situated double bonds. As can be seen from these data, the presence of a carbinol group in position 1,2 (allyl alcohol, cinnamyl alcohol) lowers considerably reactivity of the double bond. In the case of the unsaturated alcohols, methylallylcarbinol and diallylcarbinol, in which the double bond is in the 2,3-position relative to the carbinol group, the latter showing hardly any noticeable effect, their rate of thiocyanogenation approximates the thiocyanogenation rate of the corresponding hydrocarbons.

Citronellol and geraniol add thiocyanogen quite rapidly at the double bond between tertiary and secondary carbon atoms, the second double bond of geraniol not adding at all, apparently under the influence of both the carbinol group and thiocyanogen group which has been added at the more distant bond.

As the result of a study of the bromine and thiocyanogen numbers for geraniol and citronellol, which are of great importance in production of aromatic substances, the authors have succeeded in developing a method for separate determination of them in mixtures containing a saturated alcohol. The total number of double bonds in the unsaturated alcohols is determined by bromination, and the number of double bonds at a distance from the carbinol group – by thiocyanogenation. The difference between resulting bromine and thiocyanogen numbers indicates the geraniol content.

The aldehyde group displays a decelerating action which approximates that of its action upon the carboxyl group. Aldehydes with a double bond in position 1,2 – cinnamic, amylcinnamic, and others – do not add thiocyanogen at all.

With 2,6-dimethylhepten-3-al-1, having a double bond in the 2,3-position, there is observed a slow addition of thiocyanogen.

Citronellal and citral with double bonds in the 5,6-position add thiocyanogen quite rapidly. Citral, however, adds thiocyanogen only at the far double bond.

It is known from the literature that the presence of a carboxyl group lowers considerably reactivity of the double bond in relation to a number of reactants, the halogens in particular. It was found that the bromine addition reaction depends upon position of the double bond relative to the carboxyl group. Thus, for example, for crotonic acid $K = 1.8\text{-}2.4 \cdot 10^{-5}$, and for allylacetic $K = 1.4\text{-}2.3 \cdot 10^{2}$ [1].

This effect, relative to thiocyanogen, is especially large. If effect of the carbinol group disappears upon rearrangement of the double bond at the β,γ-position, then, as can be seen from the table, the effect of the carboxyl group is extended over the more remote double bonds.

The double bond in position 1,2 to the carboxyl group, as can be seen in the case of nonylenic acid and of cinnamic acid, does not add thiocyanogen at all. Butene and octahydro-β-naphthylacetic acid which have double bond in the 2,3-position hardly add thiocyanogen.

Following rearrangement of the double bond to the 3,4-position, the effect of the carboxyl group decreases: pentenic acid reacts in the same fashion as the corresponding unsaturated hydrocarbon with similar double bond.

TABLE 1

Addition of Thiocyanogen to Unsaturated Alcohols, Aldehydes, Ketones and Carboxylic Acids

Name	Percent thiocyanogenation within the time			Double bonds position relative to the functional group
	5 min.	1 hour	24 hours	
Alcohols				
Allyl alcohol	1.0	9.5	19.4	1.2
Cinnamic alcohol	1.6	6.7	19.3	1.2
Methylallyl carbinol	1.4	10.5	60.2	2.3
Diallylcarbinol	1.2	11.45	54.2	2.3
Citronellol	93.2	99.6	100.1	5.6
Geraniol	46.3	50.8	51.7	5.6 (1.2)
	92.6	101.7	100.4*	
Aldehydes				
Cinnamic aldehyde	0	0	0	1.2
a-Amylcinnamic aldehyde	0	0	0	1.2
a-Methyl-p-isopropylcinnamic aldehyde	0	0	1.4	1.2
2,6-Dimethylhepten -3-al-1	0	2.2	20.2	2.3
Citronellal	85	100.0	100.2	5.6
Citral	35.8	50.2	51.8	5.6 (1.2)
Acids and their Derivatives				
Nonylenic acid	0	0	1.8	1.2
Cinnamic acid	0	0	0	1.2
Methyl ester of Nonylenic acid	0	0	1.6	1.2
Acrylic acid nitrile	0	0	0	1.2
Butenic acid	1.2	2.4	6.9	2.3
Octahydro-β-naphthylacetic acid	–	2.2	9.2	2.3
Pentenic acid	0.7	5.7	53.2	3.4
Citronellic acid	87.5	95.5	98.4	5.6
Geranic acid	30.1	43.0	50.0	5.6 (1.2)
Nitrile of geranic acid	31.7	47.9	50.9	5.6 (1.2)
Petroselinic acid	34.6	30.8	99.4	5.6
Ketones				
Mesityl oxide	2.2	3.2	14.2	(1.2)
2-Methylhepten -4-one-6	1.8	3.5	6.4	(1.2)
Benzalacetone	0	0	5.7	1.2
β-Ionone	0	4.0	22.7*	2.4
Methylionone	6.4	15.1	35.2*	–
Isomethylionone (iralia)	5.2	11.5	24.5*	–
a-Ionone	0	1.7	6.2*	–
Isopulegone	10.9	31.0	96.5	–
Carvone	2.9	12.6	58.6**	–
6-Methylhepten -5-one-2	162	170	177.2	–
Allylacetone	5.8	26.2	110.1	–
Pseudoionone	98.5	103.1	108.2*	–
Isomethylpseudoionone	99	102.1	116.2	–

* Thiocyanogen addition takes place at one double bond.

**Calculated for one double bond.

With petroselinic and citronellic acids possessing the same remote position of double bond (position 5,6) the character of the bond is already markedly evident. Petroselinic acid, having a double bond between the secondary carbon atoms, adds about 35% thiocyanogen within 5 minutes, and citronellic acid, with a double bond between the tertiary and secondary carbon atoms, within the same time period adds 87% of thiocyanogen, by calculation.

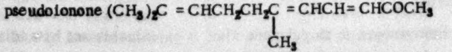
TABLE 2

Thiocyanogenation of Unsaturated Alcohols

Names and properties of substances used for the thiocyanogenation study	Theoretical thiocyanogen or bromine number	Time	Sample weight (in g)	Thiocyanogen number found	Percent of theory
Allyl alcohol: b.p. 96°; n_D^{20} 1.4139; d_4^{20} 0.8545; bromine number 276.0	275.2	5 min.	0.0887	2.7	0.98
		1 hour	0.1061	26.3	9.56
		24 hours	0.1045	53.6	19.47
Cinnamic alcohol: b.p. 129-131° (4 mm); m.p. 32.5-33°; bromine number 118.1	119.1	5 min.	0.1106	1.87	1.57
		1 hour	0.1193	7.96	6.7
		24 hours	0.1015	23.02	19.33
Methylallylcarbinol: Obtained by the Grignard reaction [2]; b.p. 120-121°; d_4^{20} 0.8440; bromine number 176.0	185.6	5 min.	0.1135	2.7	1.4
		1 hour	0.1035	19.4	10.5
		24 hours	0.0871	112.3	60.2
Citronellol: b.p. 98° (3 mm); n_D^{20} 1.4583; d_4^{20} 0.8635; bromine number 101.4	102.3	5 min.	0.0674	95.31	93.17
		1 hour	0.0878	101.95	99.67
		24 hours	0.0724	102.4	100.1
Geraniol: Purified as the calcium chloride compound; b.p. 102-104° (4 mm); n_D^{20} 1.4775; d_4^{20} 0.8835; alcohol content (by acetylation) 99.3%; bromine number 206.9	207.3	5 min.	0.0996	96.0	92.6
		0.5 hour	0.1091	102.3	98.7
		1 hour	0.0894	105.4	101.7
		24 hours	0.0926	107.2	103.4
Diallylcarbinol: Obtained by the Grignard reaction from the ethyl ester of formic acid and allyl chloride; b.p. 151.5-152.5°; d_4^{20} 0.8634; alcohol content (according to the Zerevitinoff method) 98.5%	284.5	5 min.	0.0808	3.36	1.18
		1 hour	0.0859	32.6	11.4
		24 hours	0.0665	154.35	54.2

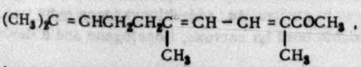
Geranic acid adds thiocyanogen quite rapidly at the double bond farther removed, and does not add at its double bond which is in the 1,2-position. A study of the addition of thiocyanogen to unsaturated acid derivatives – acrylonitrile, the nitrile of geranic acid, the diallyl ester of maleic acid, and others – indicates that the mechanism found for the free acids is also maintained by their derivatives.

As in the case of other oxygen-containing groups, the ketone group which is in the 1,2-position relative to the double bond inhibits addition of thiocyanogen. α,β-Unsaturated ketones – 6-methylhepten-3-one-2, benzalacetone, mesityl oxide – add thiocyanogen hardly at all. Ketones with conjugated double bonds in the α,β-position to the keto group: pseudoionone



$(CH_3)_2C=CHCH_2CH_2\underset{\displaystyle CH_3}{\underset{|}{C}}=CHCH=CHCOCH_3$

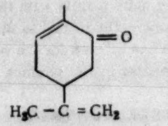
and isomethylpseudoionone



$(CH_3)_2C=CHCH_2CH_2\underset{\displaystyle CH_3}{\underset{|}{C}}=CH-CH=\underset{\displaystyle CH_3}{\underset{|}{C}}COCH_3$

, as to be expected, add thiocyanogen only at the remote double bond; for ketones with a double bond more remote from the keto group, the thiocyanogenation reaction ceases to conform to the general rules as determined for compounds of other classes.

For the two ketones, carvone and isopulegone, having identical structures, differing only in the double bond position relative to the keto group, carvone



should have added thiocyanogen at the remote double bond more rapidly than isopulegone

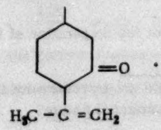


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TABLE 3

Thiocyanogenation of Unsaturated Aldehydes

Names and properties of substances used for the thiocyanogenation study	Theoretical thiocyanogen or bromine number	Time	Sample weight (in g)	Thiocyanogen number found	Percent of theory
Cinnamic aldehyde: b.p. 121° (6 mm); n_D^{20} 1.620; aldehyde content (by oximation) 100.2%; bromine number 120.3	120.9	5 min.	0.1181	0	0
		1 hour	0.1025	0	0
		24 hours	0.1002	0	0
α-Methyl-p-isopropylcinnamic aldehyde: b.p. 151-152° (12 mm); n_D^{20} 1.5810; d_4^{20} 0.9901; aldehyde content (by oximation) 98.2%.	84.9	5 min.	0.1012	2.4	2.8*
		1 hour	0.1115	3.5	4.2
		24 hours	0.1032	3.9	4.6
α-Amylcinnamic aldehyde: b.p. 138-139° (6 mm); n_D^{20} 1.5501; d_4^{20} 0.9646; aldehyde content (by oximation) 98.7%; bromine number 77.4	78.9	5 min.	0.1105	0	0
		1 hour	0.1080	0	0
		24 hours	0.1127	2.1	2.7
2,6-Dimethylhepten-3-al-1: obtained from the glycide ester [3]; b.p. 52-55° (2 mm); n_D^{20} 1.4500; d_4^{20} 0.8712; aldehyde content (by oximation) 98.3%; bromine number 107.5	114.0	5 min.	0.1219	0	0
		1 hour	0.0972	2.5	2.2
		24 hours	0.1073	23.1	20.2
Citronellal: b.p. 102° (10 mm); d_4^{20} 0.8551; aldehyde content (by oximation) 99.4%; bromine number 102.9	103.6	5 min.	0.1179	88.2	85.1
		1 hour	0.1088	102.9	99.4
		24 hours	0.0993	102.3	98.7
Citral: b.p. 103° (10 mm); n_D^{20} 1.4880; d_4^{20} 0.8882; aldehyde content (by oximation) 100.2%; bromine number 208.4	210.0	5 min.	0.1293	74.2	35.4
		1 hour	0.1163	103.2	49.1
		24 hours	0.1033	106.1	52.5

The double bond of carvone, which is situated at the 1,2-position, does not add thiocyanogen; and its presence should not affect reactivity of the double bond. It can be seen from the Table data, however, that isopulegone adds one molecule of thiocyanogen completely within 24 hours, while carvone adds only 58%.

The cause for such strange behavior of unsaturated ketones is to be sought for not only in the negative effect of the keto group upon the thiocyanogenation of the double bond, but also in the possibility of side reactions. One of the causes which may complicate thiocyanogenation of the double bond may be the formation of the enolic form of the ketone and addition of thiocyanogen at the enolic double bond. Methylheptenone with a double bond in the same position as carvone, adds thiocyanogen very rapidly in an amount exceeding 100%, no doubt due to rapid formation of the enolic form.

Apparently, addition of thiocyanogen to isopulegone also, is explainable not by addition at the usual double bond, but at the double bond of the enol form. Carvone, which is less prone to enolization, adds thiocyanogen more slowly at the enolic double bond. However, addition at the usual double bond for carvone, isopulegone and α-ionone is probably inhibited by presence of the keto group.

The above-indicated situation does not allow collection of clear-cut data on thiocyanogenation of unsaturated ketones; however, in some cases, the thiocyanogen numbers can be used to analyze unsaturated ketones. Thus, pseudoionone and pseudoisomethylionone – intermediate products in the synthesis of such aromatic substances as ionone and methylionone – react quantitatively quite readily with thiocyanogen, whereas the cyclic products of their isomerization – ionone and isomethylionone – almost fail to react at all with thiocyanogen; therefore, the method of determining thiocyanogen numbers can be used for the study and control of the pseudoionone and methylpseudoionone isomerization to the corresponding cyclic ketones.

EXPERIMENTAL

The conditions for thiocyanogenation and for the preparation of free thiocyanogen solution are given in the preceding article.

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* Negligible thiocyanogen number found, which did not increase with increase in reaction time, no doubt explicable by the presence of impurities of an unsaturated nature.

TABLE 4

Thiocyanogenation of Unsaturated Acids and Their Derivatives

Names and properties of substances used for the thiocyanogenation study	Theoretical thiocyanogen or bromine number	Time	Sample weight (in g)	Thiocyanogen number found	Percent of theory
Nonylenic acid: b.p. 95-97° (5 mm); acid content 100.3%; bromine number (0.2 N bromine solution) 100.25.	102,3	5 min.	0,1065	0	0
		1 hour	0,0984	0	0
		24 hours	0,1077	1,89	1,8
Methyl ester of nonylenic acid: b.p. 92-93° (8 mm); ester number 328,4; bromine number 91,7	93.89	5 min.	0,0942	0	0
		1 hour	0,1065	0	0
		24 hours	0,0949	1,7	1,8
Cinnamic acid: m.p. 132.5°; acid content 97.5%; bromine number 104,9	107.85	5 min.	0,1106	0	0
		1 hour	0,0966	0	0
		24 hours	0,1037	0	0
Acrylic acid nitrile: b.p. 78°	301,2	5 min.	0,0891	0	0
		1 hour		0	0
		24 hours		0	0
Butenic acid: Obtained according to Grignard from allyl iodide and carbon dioxide [4]: b.p. 163-164°; n_D^{20} 1.4260; acid content 91.1%; bromine number 81,5	185.6	5 min.	0,0900	2.2	1,2
		1 hour	0,0931	4.48	2,4
		24 hours	0,0971	12.9	6,9
Octahydro-β-naphthylacetic acid: b.p. 172-174°; (9 mm); m.p. 81-82°; acid content 99.1%; bromine number 81,5	82.25	5 min.	0,0985	0	0
		1 hour	0,0979	1,8	2,2
		24 hours	0.1025	7.6	9,2
Pentenic acid: Obtained from the diethyl ester of allylmalonic acid; b.p. 78° (4 mm); n_D^{20} 1.4310; acid content 99.2%; bromine number 159.1	159.6	5 min.	0,0979	1.07	0,7
		1 hour	0,1099	9.2	5.7
		24 hours	0,0995	84.9	53,2
Petroselenic acid: Obtained by saponification of coriander oil: m.p. 31-32°; acid content 99.1%; bromine number 56.3	56.59	5 min.	0,0990	19.56	34.6
		1 hour	0,0920	51.4	90.8
		24 hours	0.1013	56.23	99.4
Citronellic acid: Obtained by oxidation of citronellal with silver oxide [5]: b.p. 150-151° (17 mm); n_D^{20} 1.4545; acid content 100.1%; bromine number 94.3	94.45	5 min.	0.1358	82.4	87.5
		1 hour	0,1282	90.17	95.5
		24 hours	0,9908	92.9	98.4
Geranic acid: Obtained by saponification of geranic acid nitrile; b.p. 118-119° (20 mm); d_4^{20} 0.9518; acid content 98.6%; bromine number: (5 min.) 95.3; (24 hours) 188.2	190,2	5 min.	0.0936	57.3	30.1
		1 hour	0,1037	81.7	43.0
		24 hours	0.0908	95.1	50.0

The experimental data are presented in Tables 2-5, in the first columns of which are indicated the preparative method and the properties of the substances used for the thiocyanogenation study.

Method for Analysis of Geraniol-Citronellol-Isodecyl Alcohol Mixture

Thiocyanogen solution and bromine solution according to Kaufmann were added, respectively, to weighed samples, from 0.05 to 0.1 g, of the investigated mixture, and two parallel control experiments set up. 1 Hour following addition of 10 ml of 10% potassium iodide solution, the bromine excess and the thiocyanogen were titrated with 0.1 N thiosulfate solution, and the bromine and thiocyanogen numbers for the mixture determined.

Designating the difference between the bromine and thiocyanogen numbers for the mixture as A, the percent geraniol, x, is found from the ratio: $x = \frac{100A}{104}$, where: 104 - difference between the thiocyanogen and bromine numbers of geraniol and citronellol; the percent citronellol, y, is determined according to the formula: $y = \frac{e \cdot 100 - 208 \cdot x}{104}$, where: e = bromine number, x = percent geraniol, and 104 = bromine number of citronellol.

TABLE 5

Thiocyanogenation of Unsaturated Ketones

Names and properties of substances used for the thiocyanogenation study	Theoretical thiocyanogen or bromine number	Time	Sample weight (in g)	Thiocyanogen number found	Percent of theory
Benzalacetone: b.p. 128° (9 mm); m.p. 42°; bromine number (1 hour) 125.5	109.3	5 min.	0.1089	0	0
		1 hour	0.1044	0	0
		24 hours	0.1156	6.2	5.7
Mesityl oxide: b.p. 128-129° (745 mm); d_4^{20} 0.8582; n_D^{20} 1.4441; bromine number 196.8 (1 hour).	162.8	5 min.	0.0990	3.2	2.2
		1 hour	0.1013	5.3	3.2
		24 hours	0.0976	23.1	14.2
6-Methyl-3-hepten-2-one: Obtained by condensation of isovaleric aldehyde with acetone in alkaline medium [6]: b.p. 60-63° (8 mm); n_D^{20} 1.4422; d_4^{20} 0.8510; ketone content (by oximation) 98.0%	126.7	5 min.	0.1031	2.4	1.8
		1 hour	0.1100	4.4	3.5
		24 hours	0.1116	8.1	6.4
β-Ionone: b.p. 76-80° (0.1 mm); n_D^{20} 1.5204; d_4^{20} 0.9446; ketone content (by oximation) 98.9%; m.p. of semicarbazone 148-149°	83.1	5 min.	0.1139	0	0
		1 hour	0.1012	3.3	4.0
		24 hours	0.1057	18.5	22.7
Methylionone: b.p. 127-128° (10 mm); n_D^{20} 1.5004	77.5	5 min.	0.0970	4.9	6.4
		1 hour	0.1058	11.6	15.1
		24 hours	0.1080	27.2	35.2
α-Isomethylionone (iralia): b.p. 120-121° (8 mm); n_D^{20} 1.5001; d_4^{20} 0.9312	77.5	5 min.	0.0987	4.1	5.2
		1 hour	0.1008	8.9	11.15
		24 hours	0.0933	19.0	24.5
α-Ionone: b.p. 120-121° (10 mm); n_D^{20} 1.4989; d_4^{20} 0.9308; ketone content (by oximation) 99.1%; m.p. of semicarbazone 136-137°	83.1	5 min.	0.0975	0	0
		1 hour	0.1130	1.4	1.7
		24 hours	0.1296	5.2	6.2
Isopulegone: Obtained by oxidation of isopulegol [7] prepared by heating citronellal with acetic anhydride: b.p. 83-84° (9 mm); n_D^{20} 1.4670; d_4^{20} 0.9193; ketone content (by oximation) 99.2%; bromine number 132.2	105.0	5 min.	0.0979	11.4	10.9
		1 hour	0.0937	32.6	31.0
		24 hours	0.0948	101.35	96.5
Carvone: Isolated from caraway oil; b.p. 114-115° (8 mm); n_D^{20} 1.4992; d_4^{20} 0.9614	106.4	5 min.	0.1048	3.05	2.9
		1 hour	0.1013	13.4	12.6
		24 hours	0.1185	62.4	58.6
6-Methylhepten-5-one-2: Obtained by heating citral with an aqueous solution of potash; b.p. 89° (8 mm); n_D^{20} 1.4400; d_4^{20} 0.8602; ketone content (by oximation) 99.1%; bromine number 203.4	126.7	5 min.	0.1127	204.4	162.0
		1 hour	0.0934	215.1	170.0
		24 hours	0.0999	223.6	177.2
Allylacetone: Obtained by saponification of allylacetoacetic ester [8] with barium hydroxide: b.p. 128-129°; d_4^{20} 0.8469; ketone content (by oximation) 98.3%; bromine number 128.6	162.8	5 min.	0.1003	9.5	5.8
		1 hour	0.1026	43.7	26.8
		24 hours	0.1037	179.3	110.1
Pseudoionone: b.p. 128-130° (10 mm); n_D^{20} 1.5332; d_4^{20} 0.8978	83.1	5 min.	0.1085	81.8	98.5
		1 hour	0.1008	85.7	103
		24 hours	0.1170	95.0	108.2
Isomethylpseudoionone: b.p. 140-141° (10 mm); n_D^{20} 1.5221	77.5	5 min.	0.0952	76.6	99.0
		1 hour	0.0979	79.1	102.1
		24 hours	0.1173	89.9	116.2

The quantity of saturated compounds is determined as the difference between $\underline{x} + \underline{y}$ and 100%.

Example. Geraniol, citronellol and isodecyl alcohol mixture has a bromine number of 93.84 and a thiocyanogen number of 36.64. Hence, the composition of the mixture (in %) = geraniol 5.5; citronellol 80.6; isodecyl alcohol 14.5%.

SUMMARY

1. The presence of oxygen-containing functional groups (alcohol, aldehyde, ketone and carboxyl) lowers the ability of the double bond to react with thiocyanogen. The enumerated functional groups display an unusually strong effect on a double bond in the 1,2-position, to which thiocyanogen hardly adds. There is scarcely any effect of functional groups upon double bonds in the 3,4-position and further.

2. The addition reaction of thiocyanogen to unsaturated ketones is complicated by addition of thiocyanogen to the enolic form of a ketone.

3. A method for individual determinations of geraniol and citronellol in a mixture with saturated alcohol has been given.

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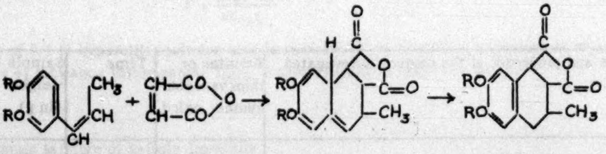
THIOCYANOGENATION OF UNSATURATED COMPOUNDS

III. THIOCYANOGENATION OF THE DOUBLE BOND SIDE CHAIN OF METHOXY- AND METHYLENEDIHYDROXY- COMPOUNDS OF THE AROMATIC SERIES

A. A. Bugorkova, L. N. Petrova and V. M. Rodionov

Aromatic compounds possessing a side allyl or propenyl group (anethole, methylchavicol, safrole, isosafrole, eugenol and isoeugenol) play a considerable role in the chemistry of perfumery materials. The bromine number method not only fails to allow separate determinations of allyl and propenyl compounds, but in some cases is also unsuited for the analysis of individual compounds because of side reactions involving replacement of nuclear hydrogen. The authors have established that introduction of the methoxy- and of the methylenedihydroxy- groups into the aromatic nucleus of related compounds increases sharply reactivity of the double bond conjugated with the phenyl radical, relative to addition of thiocyanogen, i.e., with the propenyl compounds anethole, isosafrole and isoeugenol, thiocyanogenation occurs quantitatively within 5 minutes. Compounds with an allyl side chain – such as the methoxy or methylenedihydroxy group contained in the ring (safrole, eugenol, as well as those that do not contain them (allylbenzene, propenylbenzene) – react with thiocyanogen very slowly (Table 1).

There are indications in the literature concerning a characteristic behavior of double bonds of the aromatic series which are conjugated with a double bond in the side chain and are under the influence of the methoxy and methylenedihydroxy groups. Isosafrole and methylisoeugenol, as with compounds containing a conjugated system of double bonds, give with maleic anhydride a product which rearranges into a tetrahydronaphthalene derivative [1]:



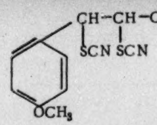
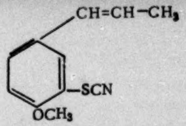
Anethole gives a normal addition product containing two molecules of maleic anhydride, i.e., it reacts as a compound with two conjugated double bond systems [2].

Data obtained by the authors on thiocyanogenation have confirmed that aromatic bonds in such methoxy- and methylenehydroxy- compounds lose their aromatic character and assume a state of conjugation with the double bond of the side chain, thus increasing reactivity of the latter.

Influence of the methoxy and methylenedihydroxy groups is also evident in reactivity of the side chain double bond which is under the negative influence of oxygen-containing functional groups.

It can be seen from data of the same table that benzalacetone and cinnamic acid do not react at all with thiocyanogen, while at the same time anisalacetone reacts quantitatively within 24 hours. p-Methoxycinnamic acid and piperonylacrylic acids add, within 24 hours, 34 and 19% respectively, of thiocyanogen.

In order to elucidate whether in actuality addition of thiocyanogen proceeds at the double bond under the authors' conditions, and not by substitution, the authors isolated the anethole thiocyanogenation product, which can be represented as:

either  or 

The anethole thiocyanogenation product separated by the authors contained nitrogen in an amount corresponding to the addition product. (10.06% nitrogen was found. For $C_{12}H_{12}OS_2N_2$ it was calculated to be 10.6).

A different concept toward thiocyanogenation of methoxylated allyl and propenyl compounds made it possible to solve the problem of individual determination of isosafrole in the presence of safrole, and isoeugenol in the presence of eugenol.

The feasibility of such determinations was demonstrated on a series of synthetically prepared mixtures, the analytical results for which are given in the experimental part.

TABLE 1

Name	Percent thiocyanogenation within the given time		
	5 minutes	1 hour	24 hours
Allylbenzene	–	2.4	58.3
Propenylbenzene	2.3	7.7	59.0
Anethole	98.8	99.4	100.2
Safrole	1.5	14.6	82.6
Isosafrole	99.9	100.6	–
Eugenol	3.7	26.0	–
Isoeugenol	98.3	99.8	101.6
Benzalacetone	–	–	5.7
Anisalacetone	2.4	20.7	100
Cinnamic acid	–	–	–
p-Methoxycinnamic acid	–	3.8	34.1
Piperonylacrylic acid	–	2.1	18.9

EXPERIMENTAL

For preparation of free thiocyanogen, see Article I. Characterizations of the investigated compounds and their thiocyanogen numbers are presented in Table 2.

Method of Determination

A weighed sample of about 0.1 g of the substance to be investigated was placed into a dry, ground-glass stoppered flask. 20 ml of thiocyanogen was added by automatic pipette. After 5 minutes, 10 ml of 10% potassium iodide solution was added to the flask, and the separated iodine titrated with 0.1 N hyposulfite solution. A parallel control experiment was carried out at the same time.

TABLE 2

Name, structure and properties of the products investigated	Bromine or thiocyanogen number, calcd.	Time	Sample weight (in g)*	Thio-cyanogen number found	Percent of theory
Allylbenzene: b.p. 156-157° b.p. 156-157°; n_D^{20} 1.5151; d_4^{20} 0.8931	135.2	5 minutes	0.1020	0	0
		1 hour	0.1007	3.18	2.4
		24 hours	0.1055	78.8	58.3
Propenylbenzene was obtained by isomerization of allylbenzene: b.p. 171°; n_D^{20} 1.5485; d_4^{20} 0.9142	135.2	5 minutes	0.1064	3.2	2.3
		1 hour	0.1002	10.4	7.7
		24 hours	0.1011	79.8	59.0
Anethole was isolated from fenchilic acid: b.p. 112-113° (9 mm); m.p. 22-22.5°	107.2	5 minutes	0.1024	106.5	98.8
		1 hour	0.1023	107.2	99.4
		24 hours	0.0962	108.1	100.2
Safrole: b.p. 99-100° (7 mm); n_D^{20} 1.5370; freezing point 11°	98.2	5 minutes	0.0973	1.48	1.5
		1 hour	0.1098	14.4	14.6
		24 hours	0.1065	81.4	82.6
Isosafrole: b.p. 103.5-104° (3 mm); n_D^{20} 1.5773	98.52	5 minutes	0.0971	98.45	99.9
		30 minutes	0.1096	98.4	99.4
		1 hour	0.1119	99.16	100.6

(Table continued on next page)

TABLE 2 (continued)

Name, structure and properties of the products investigated	Bromine or thiocyanogen number,calcd.	Time	Sample weight (in g)	Thio-cyanogen number found	Percent of theory
Eugenol was isolated from oil of eugenol basil: b.p. 124° (9 mm); n_D^{20} 1.5420; d_4^{20} 1.0702	97.3	5 minutes	0.1215	3.2	3.7
		1 hour	0.0950	25.4	26.0
		24 hours	0.1071	92.6	95.2
Isoeugenol b.p. 132° (8 mm); m.p. 16°	97.3	5 minutes	0.1104	95.6	98.5
		1 hour	0.1008	97.1	99.8
		24 hours	0.1084	98.9	101.6
Benzalacetone: b.p. 128° (9 mm); m.p. 42°; ketone content (by oximation) was 99.2%	109.3	5 minutes	0.1089	0	0
		1 hour	0.1044	0	0
		24 hours	0.1156	6.2	5.7
Anisalacetone: m.p. 73-73.5°; ketone content (by oximation) was 99.0%	92.8	5 minutes	0.1161	2.2	2.4
		1 hour	0.1208	19.2	20.7
		24 hours	0.1076	92.9	100
Cinnamic acid: b.p. 132.5°, percent content by acid number 97.5; bromine number (24 hours) 104.9	107.8	5 minutes	0.1106	0	0
		1 hour	0.0966	0	0
		24 hours	0.1037	0	0
p-Methoxycinnamic acid was obtained by condensation of anise aldehyde with malonic acid in pyridine medium [2]; m.p. 188°	89.8	5 minutes	0.1012	0	0
		1 hour	0.0974	3.45	3.8
		24 hours	0.1413	30.6	34.1
Piperonylacrylic acid: m.p. 238°	90.7	5 minutes	0.1210	0	0
		1 hour	0.1293	1.9	2.1
		24 hours	0.1118	17.2	18.9

The percent isoeugenol isosafrole and anethole (A) was calculated according to the formula

$$A = \frac{80(a-b)}{sT_{\text{calc.}}},$$

where $\underline{a}$ = quantity of 0.1 N hyposulfite solution used in titration of the control; $\underline{b}$ = titration of weighed sample; $\underline{s}$ = weighed sample of substance investigated; $T_{\text{calc.}}$ = calculated thiocyanogen number.

TABLE 3

Analysis of a Synthetic Mixture of Safrole-Isosafrole

Quantity of isosafrole (in %)	Calculated thiocyanogen number	Found thiocyanogen number				Found isosafrole (in %)			
		I	II	III	average	I	II	III	average
78.9	77.4	77.9	77.13	77.92	77.46	78.87	78.38	78.47	78.6
48.1	47.3	47.55	48.18	47.62	47.78	48.32	48.8	48.33	48.48
23.18	22.8	23.82	23.8	23.78	23.8	23.79	24.2	24.1	24.03
14.27	14.06	14.57	14.60	14.73	14.6	14.81	14.84	14.97	14.82
11.9	11.71	12.3	12.21	12.2	12.43	12.5	12.41	12.38	12.43

TABLE 4
Analysis of a Synthetic Mixture of Eugenole-Isoeugenole

Amount of isoeugenol (in %)	Calculated thiocyanogen number	Found thiocyanogen number	Found isoeugenol (in %)
90.5	88.1	88.58	91.0
75.0	73.0	73.2	75.2
71.6	69.7	70.2	72.1
48.3	47.0	47.54	48.8
19.95	19.4	20.8	21.3

SUMMARY

1. Introduction of the methoxy and methylenedihydroxy groups into an aromatic ring affects thiocyanogen addition to the double bond in the side-chain which is conjugated with the double bond of the aromatic ring.

2. A method for quantitative determination of the propenyl group in the presence of the allyl group in an aromatic compound, which contains in the ring a methoxy or methlenedihydroxy group, has been given: for isosafrole in the presence of safrole, and for isoeugenol in the presence of eugenol.

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All-Union Research Institute of Synthetic and Natural Aromatic Substances

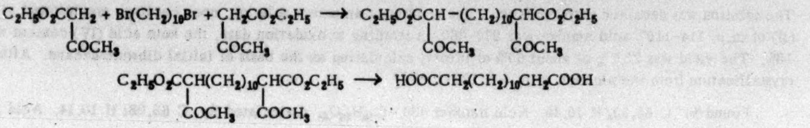
INTERMEDIATE PRODUCTS FOR SYNTHESIS OF AROMATIC SUBSTANCES

I. SYNTHESIS OF 1,14-TETRADECANDICARBOXYLIC ACID

V. M. Rodionov, E. A. Ogorodnikova, N. N. Shevyakova,
E. K. Smolyaninova and V. N. Belov

The synthesis of α,ω-dicarboxylic acids of the aliphatic series, containing 14-18 carbon atoms in the chain, offers formidable difficulties. The most convenient synthetic method for these compounds is apparently the electrolysis of the acid ester salts of α,ω-carboxylic acids of a simpler composition [1]. Recently mention was made of the synthesis by condensation of α,ω-dihalo derivatives with two molecules of acetoacetic ester, and its rupture to form the corresponding diketone [2].

There has also been developed recently a synthetic method for monosubstituted acetoacetates by direct alkylation of sodium acetoacetate resulting from the condensation of ethyl acetate (without intermediate separation of the free acetoacetate) [3]. In the present work, the authors have used this method for synthesis of the diethyl ester of 2,13-diacetyl-1,14-tetradecandicarboxylic acid (I), which was then converted into 1,14-tetradecandicarboxylic acid (II).



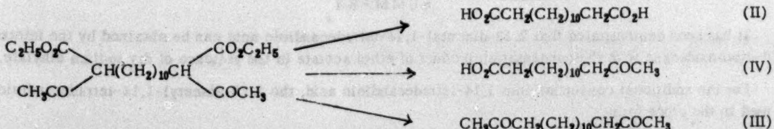
$$C_2H_5O_2C\underset{COCH_3}{CH_2} + Br(CH_2)_{10}Br + \underset{COCH_3}{CH_2}CO_2C_2H_5 \longrightarrow C_2H_5O_2C\underset{COCH_3}{CH}-(CH_2)_{10}\underset{COCH_3}{CH}CO_2C_2H_5$$

$$C_2H_5O_2C\underset{COCH_3}{CH}(CH_2)_{10}\underset{COCH_3}{CH}CO_2C_2H_5 \longrightarrow HOOCCH_2(CH_2)_{10}CH_2COOH$$

(I) (II)

Synthesis of (I) was carried out by heating 1,10-dibromodecane mixture with the condensation product of ethyl acetate (carried out in the presence of dry sodium ethylate) under conditions analogous to that described earlier for synthesis of monosubstituted acetoacetates [3]. However, in the given instance, the alkylation product (I) was not isolated in pure form since attempts to fractionate the reaction mixture (after suitable processing) resulted in extensive resinification. After distilling off excess ethyl acetate and unreacted acetoacetate from the reaction mixture (treated in the proper manner), a product resulted having: acid number 6.5-8.5; ester number 280-290; the bromine content 1-3%; oximation data corresponding to that of (I), 79-85%. This product underwent rupture.

During the process of selecting conditions for the acid split (I), the authors noted that upon heating with rather strong alkali solution, splitting occurred in both directions (the ketone split and the acid split):


$C_2H_5O_2C$
CH_3CO
$CH(CH_2)_{10}CH$
$CO_2C_2H_5$
$COCH_3$
$HO_2CCH_2(CH_2)_{10}CH_2CO_2H$ (II)
$HO_2CCH_2(CH_2)_{10}CH_2COCH_3$ (IV)
$CH_3COCH_2(CH_2)_{10}CH_2COCH_3$ (III)

It was found that heating with 15, and even as high as 33%, potassium hydroxide solution, led for the most part to the formation of hexadecan-2,15-dione (III). The diacid (II) under such conditions was formed only in small amount. Evidently keto acid (IV) was formed as well, during the splitting reactions, from a molecule of the diacetyl derivative of the diacid (I).

It was possible to obtain the diacid (II) in satisfactory yield only by using potassium hydroxide and water in a weight ratio of 5:1. In this case, the main product having been isolated from the reaction mixture after a single recrystallization from aqueous alcohol (1:1), had a m.p. of 112-116° and represented, according to the analytical data (determination of the acid number and the keto group), 80-85% diacid (II) in admixture with 20-15% keto acid (IV). The yield of diacid amounted to about 60% of theory, calculating on the basis of dibromodecane taken for the condensation reaction. After purification with diethyl ether, the diacid (II) melted at 122-123°; keto acid was not present, and it was possible only in some cases to detect a negligible amount. Such purification accounted for the losses: yield (II) constituted 30-33%, also calculating on the basis of dibromodecane.

EXPERIMENTAL

330 g of the reaction mixture*, obtained by condensation of ethyl acetate in the presence of dry sodium ethylate with 45 g of dibromodecane (m.p. 43-44°) was placed in a 750 ml flask, equipped with thermometer, mercury seal and stirrer. The reaction mixture was stirred thoroughly, maintaining a temperature of 78-80° for 40-45 hours, treated with 200 ml of water (to complete dissolution of precipitate) and the upper layer which separated was washed with a solution of sodium chloride to the point of neutral reaction.

After distilling off the excess ethyl acetate, the unreacted acetoacetate was removed under vacuo. The residue, amounting to 58-62 g (its characterization being given in the general section) underwent acid splitting. For this purpose, 150 g of finely-powdered potassium hydroxide and 30 ml of water were placed in a 750 ml flask equipped with stirrer and dropping funnel. The flask was immersed in an oil bath in such manner that the level of the reaction mixture was somewhat lower than that of the oil level in the bath (in order to avoid crystallization of the reaction product upon the cold walls of the flask). At a temperature of 95-100°, the condensation product (I) was added to alkali dropwise over a period of 1 hour, without allowing temperature to exceed 110°. The reaction mixture was then heated at the same temperature for about 2 more hours. By that time, the reaction mixture had solidified considerably, and after cooling to room temperature, was almost solid. The flask contents were treated with 500 ml of water and then acidified with hydrochloric acid (1:1) to an acid reaction with Congo red. The crystallized product (II) which resulted was filtered with suction and dried to constant weight at a temperature of 50-60°. There resulted 35-37 g of diacid (II) which was contaminated with resinous impurities and which contained a certain amount of keto acid (IV). The product was dissolved in hot 50% alcohol, in which a portion of the impurities was insoluble. The solution was decanted onto the filter. The resulting transparent solution, upon cooling, precipitated as crystals (II) of m.p. 114-116°; acid number was 370-380. According to oxidation data, the keto acid (IV) content was about 15%. The yield was 23.2 g or about 60% of theory, calculating on the basis of initial dibromodecane. After recrystallization from the alcohol, m.p. was 123-124°.**

Found %: C 65.30; H 10.45. Acid number 430. $C_{14}H_{26}O_4$. Calculated %: C 65.08; H 10.14. Acid number 434.

The keto acid (IV) isolated from the reaction mixture had a m.p. of 75-76°.

Found %: C 70.39; H 11.11. Acid number 214.1. $C_{15}H_{28}O_3$. Calculated %: C 70.27; H 11.01. Acid number 218.7.

Purification of (II) can be effected by its conversion to the dimethyl ester. A mixture of 17.5 g of technical (II), 22 g of methyl alcohol, and 4 g of concentrated H_2SO_4 was left at room temperature. After 2-3 days, crystals of the dimethyl ester separated, and were distilled in vacuo. There resulted 7.8 g of the dimethyl ester with b.p. 185-188° (at 6 mm); after recrystallization from alcohol, m.p. 42.5-43.5°.*** On saponification of the ester, there resulted acid (II) with m.p. 122-123°; yield was almost quantitative.

SUMMARY

It has been demonstrated that 2,13-diacetyl-1,14-tetradecandioic acid can be obtained by the interaction of 1,10-dibromodecane with the condensation product of ethyl acetate in the presence of dry sodium ethylate.

For the additional conversion into 1,14-tetradecandioic acid, the 2,13-diacetyl-1,14-tetradecandioic acid can be used in the crude form.

By carrying out the splitting reaction under very rigorous conditions (weight ratio of KOH to water = 5:1), there results the diacid containing about 15% of keto acid, from which separation can be effected by recrystallization. However, if 15 or 33% KOH solution is used, the principal product of rupture is found to be the hexadecane-2,15-dione.

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* This amount corresponds to 0.50-0.55 mole of sodium ethylate used for condensation.

** According to the literature data: m.p. 123° [4]; 124° [5].

*** According to the literature data, m.p. 41° [5].

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INTERMEDIATE PRODUCTS FOR SYNTHESIS OF AROMATIC SUBSTANCES

II. HEXADECANE-2,15-DIONE SYNTHESIS

V. M. Rodionov, N. E. Kologivova, E. A. Ogorodnikova and V. N. Belov

In the preceding article [1] which described conditions for synthesis of 1,14-tetradecandioic acid by acid splitting of the condensation product between dibromodecane and two molecules of acetoacetic ester, it was observed that in addition to the acid split, there also occurred in practically all instances the ketone split, leading to formation of the corresponding keto acid and hexadecane-2,15-dione.

Data have been given for synthesis of hexadecane-2,15-dione by rupture of the above-mentioned condensation product with alcoholic potassium hydroxide solution at room temperature for 5 days [2, 3]. The yield of product, m.p. 83-84°, according to the data was 30% of theory.

Because of the fact that this diketone is an intermediate in the synthesis of certain macrocyclic ketones [4, 5], the authors carried out a series of experiments which had as their object the task of finding conditions for securing maximum yield of hexadecane-2,15-dione in the reaction indicated. Rupture of the condensation product indicated above was carried out in acid, alkaline and neutral media. The reaction time and the concentrations of reactants were varied in separate experiments. As a result of the work carried out, it was established that by heating in an acetic acid medium of varying concentration (up to that of glacial acetic acid), the product did not undergo change. Using sodium hydroxide in the concentration range 2 to 33%, ketonic rupture proceeded rapidly, leading to the formation of diketone in good yield (see Experimental). Hexadecane-2,15-dione was also formed by heating the condensation product in an autoclave with water for 5 hours at a temperature of 200°. In this case, however, the process was accompanied by considerable resinification.

EXPERIMENTAL

The best results were obtained by carrying out the reaction in the following manner. 29 g of the dibromodecane condensation product with acetoacetic ester, prepared according to the method indicated in article I [1], 120 ml of alcohol, and a 10% aqueous solution of sodium hydroxide were placed in a 200 ml flask equipped with reflux condenser, and the total heated for 1 hour. The diketone formed by cooling the reaction mixture crystallized, which was easily separated. 13.2 g of crystalline product resulted, with m.p. 70-75°.

TABLE

Quantity		Reaction time (in hours)	Quantity of resulting diketone (in g)	Melting point of the diketone (in °C)	Yield of diketone (in % of theory recalculated to dibromodecane)
of condensation product taken (in g)*	Concentration of NaOH or CH_3COOH				
10.0	25 g 10% aqueous NaOH	1	2.6	81-82.5	40.6
10.0	25 g 10% aqueous NaOH	3	2.59	80-82	40.4
10.0	25 g 10% aqueous NaOH	0.5	1.2	83-84	18.7
5.0	68 g 2% aqueous NaOH	1	0.68	81-83	21
10.0	40 g 10% CH_3COOH	1	Initial product isolated unchanged		
10.0	40 g 10% CH_3COOH	6			
10.0	30 ml glacial acetic acid	1			
10.0	50 g 5% aqueous alcoholic NaOH	1	2.42	80-82	37.7
10.0	40 g 10% aqueous alcoholic NaOH	1	2.85	80-82	53.8
10.0	20 ml water	5 at 200°	3.3	71-75	62 (Resinous product)

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* The product prepared under the conditions described earlier was used.

Yield amounted to 71% recalculated to dibromodecane taken for the condensation reaction. After double recrystallization from aqueous alcohol (1:1), the hexadecane-2,15-dione had a m.p. of 85-86° which remained unchanged upon additional recrystallizations. Yield of recrystallized diketone constituted about 50% of theory, calculating again on the basis of dibromodecane.

Found %: C 75.24, 75.45; H 11.85, 11.82. $C_{16}H_{30}O_2$. Calculated %: C 75.54; H 11.88%.

Semicarbazone m.p. 198-199°. According to the literature data [3], m.p. 199-200°.

Results of experiments under other conditions are given in the Table.

SUMMARY

On rupture of the condensation product of 1,10-dibromodecane with two molecules of acetoacetic ester with 10% aqueous-alcoholic solution of sodium hydroxide, there results hexadecane-2,15-dione in yield up to 71% of theory (calculating on the basis of dibromodecane taken for condensation). Yield of pure product with m.p. 85-86° constitutes about 50% of theory.

Under such conditions no products of acid cleavage are formed.

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* See Consultants Bureau Translation, page 1927.

NEW DATA ON THE PROBLEM OF γ-CHLOROACETOACETIC ESTER CONDENSATION AND THE SYNTHESIS OF δ-CHLOROLEVULINIC ACID

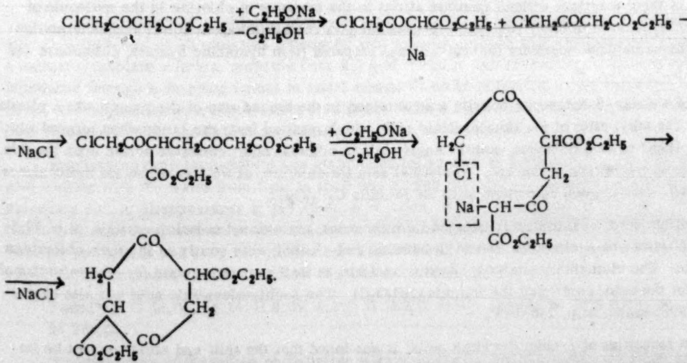
V. M. Rodionov and M. A. Gubareva

The purpose of this investigation was preparation of δ-chlorolevulinic acid, which is not described in the literature. This latter compound can be used as the starting material for synthesis of certain important amidazole derivatives of histidine, histamine, and other types.

Of the halogenated levulinic acid derivatives β-chloro- and β-bromo-levulinic acids prepared by interacting levulinic ester with the corresponding halides are known, as well as the α- and β-bromolevulinic acids, prepared by the addition of hydrogen bromide to acetylacrylic acid, and by bromination of α-angelicolactone [1]. X-Monochlorolevulinic acid, so-called [2], synthesized by reaction of phosphorus pentachloride with levulinic acid, was found, so far as can be assumed from the excessive chlorine content and liquid state of the reaction product, to be a mixture of the monochlorolevulinic acid with some disubstituted product.

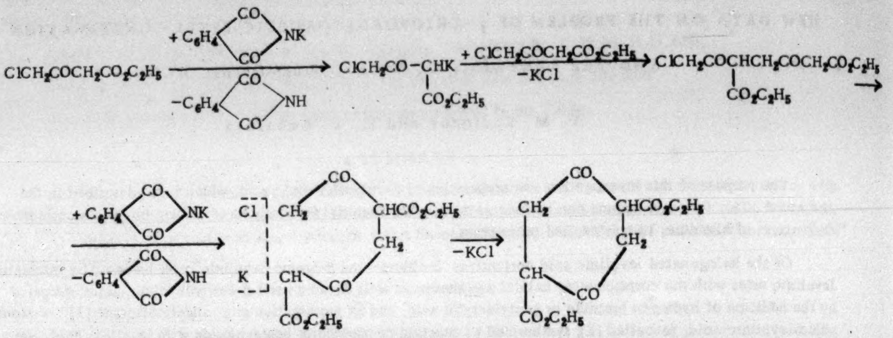
Since levulinic acid is readily obtained by condensation of acetoacetic and monochloroacetic esters [3], an attempt was made to prepare δ-chlorolevulinic acid by interacting γ-chloroacetoacetic ester with the monohalogenated acetate prepared according to the procedure described by Rodionov and Polunina [4]. The γ-chloroacetoacetic ester necessary for condensation was prepared according to the excellent procedure of Aleksandrov, by reacting magnesium with chloroacetic ester [5].

By carrying out condensation of chloroacetoacetic ester with chloroacetic ester in the presence of sodium ethylate, a nicely-crystallizing compound was isolated with m.p. 127°, plus a large amount of viscous, considerably resinified oil. Upon investigation, the crystalline substance was found to be the succinic ester. The same product resulted by similar treatment of γ-chloroacetoacetic ester without chloroacetic ester. This implied that the condensation reaction apparently proceeds according to the following scheme:



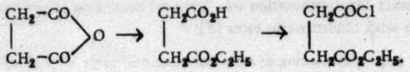
The succinyl succinate ester obtained from γ-chloroacetoacetic ester did not differ, according to its elementary analysis, its molecular weight, and other properties, from the compound described earlier in the literature [6].

In addition, in order to avoid formation of succinylsuccinate ester, an attempt was made to replace the chlorine of γ-chloroacetoacetic ester by the phthalylamino group $C_6H_4\left\langle\begin{matrix}CO\\CO\end{matrix}\right\rangle N-$. Phthalylaminoacetoacetic ester, upon condensing with chloroacetic ester and subsequent saponification, should have given δ-aminolevulinic acid. However, upon reacting potassium phthalimide with γ-chloroacetoacetic ester, there also occurred formation of succinylsuccinate ester. Thus, potassium phthalimide in the given case was found to function only as a condensing agent.



The succinylsuccinate ester resulting after purification possessed a m.p. of 127.5°. Yield was 56.4% of theory. A sample mixed with the product of the preceding synthesis did not give depression in melting point.

In addition, the δ-chlorolevulinic acid needed by the authors was obtained in high yield (90% of theory) according to the method of Arndt-Eistert [7]. For this purpose, succinic acid, through its anhydride, was converted into this acid ester and into its chloroanhydride:



The monochloroanhydride gave diazoketone with diazomethane, converting into the δ-chlorolevulinic acid ester when reacted with hydrogen chloride.

$$ClCOCH_2CH_2CO_2C_2H_5 + CH_2N_2 \rightarrow N_2CHCOCH_2CH_2CO_2C_2H_5 \xrightarrow{HCl} ClCH_2COCH_2CH_2CO_2C_2H_5.$$

The mechanism of these reactions without question attests to the presence of chlorine in the molecule of chlorolevulinic ethyl ester, located in the δ position, and does not give reason to expect simultaneous formation of other isomers. The diazomethane necessary for synthesis was prepared from hydrazine hydrate, chloroform and potassium hydroxide [8].

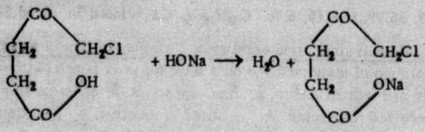
The ethyl ester of 4-diazo-3-butanoncarboxylic acid obtained in the second step of the process was a pleasant-smelling, mobile oil. The ethyl ester of δ-chlorolevulinic acid, which resulted from the latter when reacted with hydrogen chloride, was found to be a colorless, mobile liquid with an ethereal odor; corrosive action upon the skin, especially upon the mucous membrane of the eye. Analytical data for chlorine, as well as values for molecular refraction of the compound, were in good agreement with the formula $C_7H_{11}O_3Cl$.

The δ-chlorolevulinic acid, quantitatively isolated from the ester, represented colorless crystals, m.p. 72.5-73.5°, readily soluble in water and acetic acid, less so in benzene and alcohol, very poorly so in ether, chloroform and carbon tetrachloride. The elementary analysis, chlorine analysis, as well as titration data for determination of the equivalent weight for the acid, confirmed the formula $C_5H_7O_3Cl$. The δ-chlorolevulinic acid was also characterized through its semicarbazone, m.p. 148-149°.

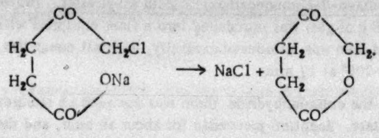
Upon studying the properties of δ-chlorolevulinic acid, it was found that the salts and amide cannot be isolated from it. Thus, upon neutralization of alcoholic and aqueous solutions of the acid with dilute solutions of alkalies and soda, upon evaporation, the mineral salts were produced instead of δ-chlorolevulinic acid salt – chlorides – and an oil which did not possess acid properties, and evidently represented the lactone of δ-hydroxylevulinic acid.

It should be considered that rupture of the chloride, with formation of the heterocyclic compound, occurs only with heating and evaporation, since only after heating of the neutral solution does silver nitrate give a precipitate of silver chloride. The reaction course in such case, apparently, corresponds to the following scheme:

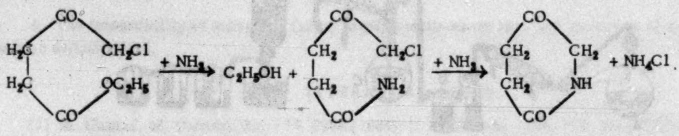
1) In the solution, upon neutralization at room temperature the salt is formed



2) During evaporation, there occurs ring closure of the salt solution



A similar course of reaction has also been observed in other cases. Thus, while attempting to obtain the δ-chlorolevulinic acid amide from chloroanhydride and ethyl ether, there was isolated quantitatively ammonium chloride and a highly hygroscopic oil, crystallizing with difficulty over P_2O_5 and again melting rapidly in air. It can be assumed that in this case as well, there proceed reactions with formation of a six-membered ring, namely:



The second stage, with formation of ammonium chloride crystals in the reaction mixture, proceeds during distillation of the alcohol. The oil resulting in this case, containing nitrogen, was not investigated because of its extreme hygroscopicity and small amount, and attempts to convert it to the semicarbazone and picrate were unsuccessful.

EXPERIMENTAL

1. Condensation of γ-chloroacetoacetic ester by means of sodium ethylate. 15 g of γ-chloroacetoacetic ester (b.p. 107-108° at 15 mm) was introduced into a flask equipped with condenser and calcium chloride tube, and a sodium alcoholate solution, prepared from 2.1 g of metallic sodium and 60 ml of absolute ethyl alcohol, was introduced through a dropping funnel in small amounts with hand stirring. Heat evolution from the mixture took place, with separation of a white, fluffy precipitate, with a simultaneous change in color of the reaction mixture from colorless to pink and then to red-brown.

Reaction mixture temperature was maintained for an hour at a temperature not exceeding 40°, for which purpose cooling with ice water from time to time was carried out, and the mixture then heated on a water bath, not exceeding 60°, to disappearance of the alkaline reaction. After termination of heating, there separated from the reaction mixture cooled to room temperature, a precipitate which was filtered off. Sodium chloride was extracted from the precipitate and 4.5 g of colorless crystals, consisting of succinylsuccinate ester resulted, m.p. of which was 127° after washing with absolute alcohol. Yield was 38.6% of theory.

Found %: C 56.01, 56.14; H 6.39, 6.19. M 264.2, 253.5. $C_{12}H_{16}O_6$. Calculated %: C 56.25; H 6.25. M 256.25.

2. Interaction of potassium phthalimide with γ-chloroacetoacetic ester. 50 ml of xylene was introduced into a flask equipped with reflux condenser and calcium chloride tube, followed by 6 g of potassium phthalimide in small portions and 5 g of γ-chloroacetoacetic ester of b.p. 104-107° at 14 mm.

Reaction was carried out for about a half-hour at room temperature, and then the reaction mixture was heated on a water bath at 60°. Since the flask contents resinified noticeably upon heating, the mixture, therefore, was left at room temperature for the night. On the following day, the precipitate (8.6 g) was filtered off from the reaction mixture, the former consisting of potassium chloride, phthalimide (m.p. 231°) and potassium phthalimide. Xylene was distilled off from the filtrate with steam, and there resulted a residue of 2.2 g succinylsuccinate ester, with m.p. 127°. A sample mixed with ester prepared in a preceding experiment did not give depression in melting point.

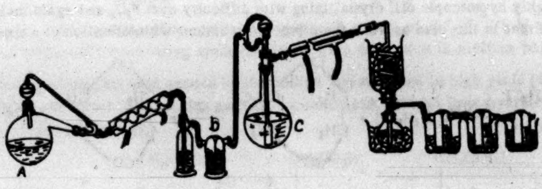
The yield of succinylsuccinate ester was 56.4% of theory.

Found %: C 55.98, 55.99; H 6.10, 5.75. $C_{12}H_{16}O_6$. Calculated %: C 56.25; H 6.25.

3. Synthesis of δ-chlorolevulinic acid ethyl ester. a) Preparation of an ethereal solution of diazomethane. To synthesize an ether solution of diazomethane on a standard work bench (without draft), using nitrogen obtained from ammonium chloride and sodium nitrite, a fine apparatus for efficient trapping of toxic gas was assembled (see Figure). Nitrogen received from retort A, is dried in receiver, B. Reaction is carried out in flask, C, at such a rate that the diazomethane forming can be absorbed completely in the first three absorption flasks.

b) Synthesis of 4-diazo-3-butanoncarboxylic acid ethyl ester. 700-800 ml of filtered diazomethane ether solution containing about 8 g of gas, was introduced into a flask equipped with calcium chloride tube. The solution was precooled to −5° and then was introduced carefully, in small quantities, into 15 g of succinic acid chloroanhydride ethyl ester, b.p. 102-105° at 17 mm.

During addition of the chloroanhydride, there was observed an energetic evolution of nitrogen, and formation of a white, flaky precipitate. Reaction proceeded for about an hour, and then ceased completely.



The reaction mixture was left for the night at room temperature, the flask being sealed with a calcium chloride tube. On the following day the reaction mixture, containing a small residue of diazomethane, was filtered and the ether distilled out until $\frac{1}{4}$ of the original volume was reached. The residue containing ethyl ester of 4-diazo-3-butanoncarboxylic acid was decomposed with dry hydrogen chloride.

c) Synthesis of the ethyl ester of δ-chlorolevulinic acid. The resulting ester solution of 4-diazo-3-butanoncarboxylic acid was decomposed with dry hydrogen chloride at a temperature of −5 to −10°. At the start of saturation, very violent evolution of nitrogen proceeded, after which the nitrogen evolution proceeded more mildly. Saturation was complete after 4-5 hours. After termination of the saturation, solvent was partially distilled out of the reaction mixture in order to remove excess hydrogen chloride. 150-200 ml of fresh ester was added to the residue, the solution washed twice with water, then with 5% soda solution, and then with water to a neutral reaction of the wash waters. The wash waters were also extracted with ether, the ether solution washed to a neutral reaction, and this extract added to the main ether solution. The ether solution was dried over calcium chloride. After distilling off the solvent, 15.6 g (96.3% of theory) of crude product resulted − the ethyl ester of δ-chlorolevulinic acid, in the form of a dark-red oil, which was purified by double distillation in a flask with dephlegmator. B.p. was 115-120° at 10 mm (137-140° at 20 mm, 230-235° at 760 mm). Yield of pure ester was 14.63 g (90% of theory).

The resulting ester was an oil with faint odor, corrosive action on the skin, and especially upon the mucous membrane of the eye. It was readily soluble in alcohol, ether, chloroform, and was insoluble in water.

Found %: Cl 19.88, 19.94. $C_7H_{11}O_3Cl$. Calculated %: Cl 19.86.

4. Synthesis of δ-chlorolevulinic acid. 5 g of the ethyl ester of δ-chlorolevulinic acid and 50 ml of hydrochloric acid solution (1: 3) were placed in a flask equipped with reflux condenser and the mixture heated on a water bath to complete dissolution of the oil. The resulting solution was evaporated on a water bath almost to dryness. 25 ml of distilled water was added, and evaporation again carried out. Treatment of the dry residue with water, for complete removal of hydrogen chloride, was repeated until vapors of hydrochloric acid were hardly noticeable. Upon cooling the evaporated solution, 4 g of unpurified δ-chlorolevulinic acid resulted, which melted at 67-68°. The yield of crude acid was almost quantitative.

After two recrystallizations from benzene, 3.7 g of δ-chlorolevulinic acid resulted: crystalline platelets, 72-73.5°. Yield of purified acid was 88%.

Found %: C 40.10, 40.04; H 4.79, 4.64; Cl 23.91, 23.90; g-equiv. 149.2, 150.4. $C_5H_7O_3Cl$. Calculated %: C 39.87; H 4.69; Cl 23.57; g-equiv. 150.46.

5. Synthesis of the semicarbazone of δ-chlorolevulinic acid. According to Zelinsky [9], a mixture was prepared from 6.7 g of semicarbazide hydrochloride, 5.6 g of sodium acetoacetate and 20 ml of water. 1 g of the δ-chlorolevulinic acid was dissolved in 5 ml of water and mixed with 5 ml of the prepared mixture (double amount with respect to theory being taken). Needle crystals of the semicarbazone precipitated very rapidly. After three recrystallizations from methyl alcohol, m.p. was 148-149° (with decomposition). The yield amounted to 80% of theory.

Found %: N 20.31, 20.62. $C_6H_{10}O_3N_3Cl$. Calculated %: N 20.25.

SUMMARY

1. It has been established that γ-chloroacetoacetic ester reacts with sodium ethylate forming the succinylsuccinate ester.

2. It has been found that when attempt is made to condense γ-chloroacetoacetic ester with potassium phthalimide, there is also formed the succinylsuccinate ester, and not the δ-phthaliminoacetoacetate.

3. A satisfactory method for synthesis of δ-chlorolevulinic acid and ester has been developed, not described hitherto in the literature.

4. The impossibility of separating (under usual conditions) the salts and the amide of δ-chlorolevulinic acid has been demonstrated.

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and the I. V. Stalin 2nd Moscow State Medical Institute,
Organic Chemistry Department

Found %: C 40.10, 39.94; H 4.76, 4.64; Cl 32.82, 32.98; g-equiv. [illegible] [illegible]. Calculated %: C 39.89; H 4.59; Cl 33.87; g-equiv. 120.46.

6. Synthesis of the semicarbazone of β-chloroisovaleric acid. According to [illegible] was prepared from 0.1 g of semicarbazide hydrochloride, [illegible] g of sodium acetate and [illegible] β-chloroisovaleric acid was dissolved in 5 ml of water and mixed with [illegible] (double amount with respect to theory being taken). Needle crystals of the semicarbazone [illegible] these crystals (filtered from mother liquor), m.p. [illegible] (with decomposition). Yield [illegible] of theory.

Found %: N 20.21, 20.53. [illegible] Calculated %: N [illegible]

SUMMARY

1. It has been established that [illegible] ester reacts with sodium [illegible] forming [illegible] ester.

2. It has been found that when attempt is made to condense γ-chloroacetoacetic ester with potassium phthalimide, there is also formed the [illegible] ester, and not the [illegible].

3. A satisfactory method for synthesis of β-chloroisovaleric acid and [illegible] has been developed, not described hitherto in the literature.

4. The impossibility of separating (under [illegible]) the [illegible] of β-chloroisovaleric [illegible] has been demonstrated.

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Received May 20, 1948 [illegible]
[illegible] Department of Chemistry, and [illegible] Institute, Organic Synthesis Laboratory

CHARACTERIZATION OF β-(α-NAPHTHYL)-β-ALANINE

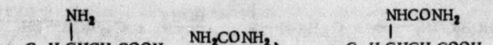
V. M. Rodionov, L. V. Antik and N. A. Kravchenko

β-(α-Naphthyl)-β-aminopropionic acid, certain of its acyl derivatives, and their amides have been described earlier [1].

Synthesis of β-(α-naphthyl)-β-alanine differs somewhat from the usual method, and was carried out by heating α-naphthaldehyde in a solution of glacial acetic acid with slight excess of malonic acid (25%) and a large excess of ammonium acetate (125-250%). Naphthylaminopropionic acid separates readily from the resulting by-product, α-naphthylacrylic acid, either in the hydrochloride form [1], or by careful treatment of a mixture of the two compounds with ethyl ether, which dissolves only the naphthylacrylic acid.

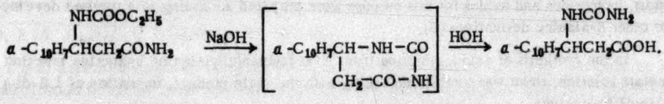
A modification was introduced [2] in the method of preparing initial α-naphthaldehyde, resulting from heating of α-chloromethylnaphthalene with hexamethylenetetramine, which consists of replacing water-alcohol medium with 50% acetic acid solution. The yield of α-naphthaldehyde was accordingly increased from 30 to 75%.

β-(α-Naphthyl)-β-aminopropionic acid gives many reactions characteristic for the β-amino acids. Thus, when heated with urea, it forms readily the corresponding β-ureido acid:



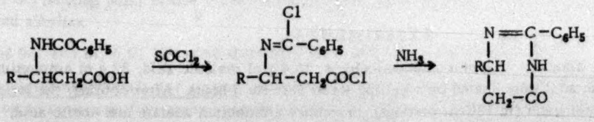
$$\alpha\text{-}C_{10}H_7\overset{\overset{NH_2}{|}}{C}HCH_2COOH \xrightarrow{NH_2CONH_2} \alpha\text{-}C_{10}H_7\overset{\overset{NHCONH_2}{|}}{C}HCH_2COOH.$$

The same compound is formed when the amide is heated with alkali, according to the reaction proposed by Zvorykina and Rodionov [3]:



$$\alpha\text{-}C_{10}H_7\overset{\overset{NHCOOC_2H_5}{|}}{C}HCH_2CONH_2 \xrightarrow{NaOH} \left[\alpha\text{-}C_{10}H_7\begin{array}{l}CH-NH-CO\\ |\qquad\qquad |\\ CH_2-CO-NH\end{array}\right] \xrightarrow{HOH} \alpha\text{-}C_{10}H_7\overset{\overset{NHCONH_2}{|}}{C}HCH_2COOH.$$

More complex is the course of reaction for formation of 2-phenyl-4-alkyl(aryl) -6-oxotetrahydropyrimidines [4]. The method for deriving these compounds consists in the interaction of N-benzoylated β-amino acids with thionyl chloride, and subsequent treatment with ammonia:



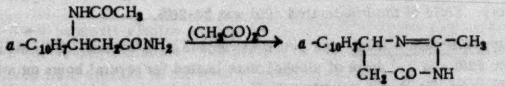
$$\begin{array}{l}NHCOC_6H_5\\ |\\ R-CHCH_2COOH\end{array} \xrightarrow{SOCl_2} \begin{array}{l}\qquad Cl\\ \qquad |\\ N=C-C_6H_5\\ |\\ R-CH-CH_2COCl\end{array} \xrightarrow{NH_3} \begin{array}{l}N=\!=C-C_6H_5\\ |\qquad |\\ RCH\quad NH\\ |\qquad |\\ CH_2-CO\end{array}$$

It was found that during the normal course of reaction with N-benzoylnaphthylalanine, there occurred chiefly a large amount of resinification and desamination; it was possible to isolate only a small quantity of naphthylacrylic acid amide.

$$\alpha\text{-}C_{10}H_7CH=CH-CO_2H \xrightarrow{SOCl_2} \alpha\text{-}C_{10}H_7CH=CHCOCl \xrightarrow{NH_3} \alpha\text{-}C_{10}H_7CH=CHCONH_2.$$

The corresponding 2-phenyl-4-naphthyl-6-oxotetrahydropyrimidine resulted in small yield only when the N-benzoylnaphthylalanine was treated with thionyl chloride in benzene solution, with subsequent amination, or upon heating the amide of the benzoylated alanine derivative with benzoyl chloride or acetic anhydride.

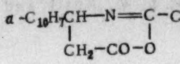
2-Methyl-4-naphthyl-6-oxotetrahydropyrimidine formed very smoothly by reaction of N-acetylnaphthylalanine with acetic anhydride:



$$\alpha\text{-}C_{10}H_7\overset{\overset{NHCOCH_3}{|}}{C}HCH_2CONH_2 \xrightarrow{(CH_3CO)_2O} \alpha\text{-}C_{10}H_7\begin{array}{l}CH-N=\!=C-CH_3\\ |\qquad\qquad\ |\\ CH_2-CO-NH\end{array}.$$

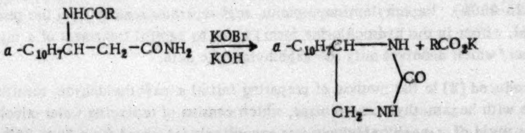
Conversion of naphthyl-β-alanine to 4-α-naphthylglyoxalidone was realized in two ways.

1) Interacting amides of acylated alanines with alkaline hypobromites according to the Hofmann reaction. The N-acyl derivatives, and their amides required for this purpose, were prepared by the method described earlier. It should be mentioned here that when heating naphthylalanine with acetic anhydride under the conditions in question [1], there was established the formation of a by-product (m.p. 234°), apparently an oxazine derivative:

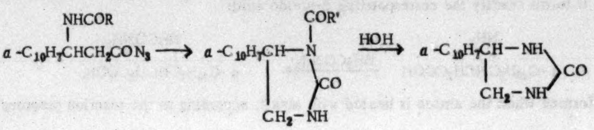


Investigation of this compound is still underway.

Interaction of acylated amides with hypobromite proceeds, as a rule, with simultaneous rupture of the acyl group:

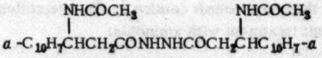


2) Heating N-acylated azides in dry benzene according to the Curtius reaction. Good yield results of readily hydrolyzable N-acylated α-naphthylglyoxalidone:



Esters, hydrazides and azides for this purpose were prepared according to a method developed earlier by the authors for other β-alanine derivatives [5].

In the synthesis of azide, resulting from N-acetylnaphthylalanine hydrazide reaction with sodium nitrite in acetate solution, there was established, along with the main product, formation of 1,2-di-[N-acetyl-β(α-naphthyl)-β-alanyl] hydrazine:



$$\alpha\text{-}C_{10}H_7\underset{}{\overset{\overset{\displaystyle NHCOCH_3}{|}}{C}}HCH_2CONHNHCOCH_2\overset{\overset{\displaystyle NHCOCH_3}{|}}{C}HC_{10}H_7\text{-}\alpha$$

EXPERIMENTAL

β-(α-Naphthyl)-β-alanine. 16 g of α-naphthaldehyde, 13.4 g of malonic acid, 32 g of ammonium acetate and 40 g of glacial acetic acid were heated on a boiling water bath for 7 hours. After cooling, the solidified mass was washed twice with cold water (in 130 ml portions), to remove ammonium acetate and acetic acid. The water extract was brought to a weakly alkaline reaction with soda. Upon standing, 4 g of amino acid precipitated with m.p. 214-215°.

The residue, after treatment with water, represented a mixture of β-amino acid and α-naphthylacrylic acid, which can be separated by either of two methods.

1) Dilute hydrochloric acid is poured over the mixture and allowed to stand for 2-3 hours, after which it is filtered off from unsaturated acid, the precipitate washed with dilute hydrochloric acid and water. The acid filtrate and wash waters are combined, extracted with ether, and the acid aqueous solution evaporated to dryness. The amino acid hydrochloride results.

2) The residue is separated by prolonged treatment (over 120 hours) with ether in a Soxhlet apparatus. β-Amino acid does not dissolve in ether and can be filtered off. The total yield of β-amino acid was 13.5-16.6 g, i.e., about 60-74% of theory. Yield of the unsaturated acid was 20-26%.

β-(α-Naphthyl)-β-ureidopropionic acid. 0.2 g of β-(α-naphthyl)-β-alanine, 0.6 g of urea, and 4 ml of water 1.5 ml of 1 N-hydrochloric acid and 2-3 drops of alcohol were heated for several hours on a boiling water bath. After completion of the reaction, the liquid was filtered off, extracted twice with ether and acidified with strong hydrochloric acid. The transparent liquid was rapidly poured off from the resin which formed and rolled up into a ball, from which, after 10-15 minutes, there precipitated out large crystals of the ureido acid. The melting point was not sharp; the substance melted at 105-110°, evidently in its own water of crystallization, solidified, and then melted again at 163-165°. The yield was 0.18-0.19 g (about 68%). After recrystallization from alcohol, the m.p. was 170-171°. The substance crystallized with 2 molecules of water.

Found %: Water of crystallization 12.25. $C_{14}H_{14}O_3N_2 \cdot 2H_2O$. Calculated %: H_2O 12.24.

The same compound was obtained by heating β-(α-naphthyl)-β-(N-carboethoxy)alanine with a weak alkaline solution. 0.15 g of urethane amide was heated with 7.5 ml of 5% sodium hydroxide to complete solution, filtered from slight turbidity, and the filtrate acidified with hydrochloric acid. After prolonged standing, a coarse crystalline precipitate (0.09 g) separated, which melted, first at 105-110°, and then at 163-165°. The preparation, recrystallized from alcohol, melted at 170-171°, and did not give depression of melting point in mixed sample with the above-described compound.

Naphthylcarboethoxyalanine was prepared by standard procedure. 2 g of β-(α-naphthyl)-β-alanine was dissolved in 25 ml of 2% sodium hydroxide solution, cooled with ice water, and 1.5 g of chlorocarbonic ester introduced with vigorous stirring. The reaction liquid was stirred for another 40 minutes and acidified with hydrochloric acid to a Congo red reaction. The separated precipitate was filtered off and dried. Yield was 1.85 g. M.p. 168-173°. For analysis, the carboethoxy compound was dissolved in aqueous alcohol and shaken several times with ether. The water-alcoholic solution was concentrated in vacuo. Upon cooling, a pure substance separated in the form of small needles with m.p. 175-177°.

Found %: N 5.20. $C_{16}H_{17}O_4N$. Calculated %: N 4.87.

N-Acetyl-β-(α-naphthyl)-β-alanine. 10 g of β-(α-naphthyl)-β-alanine was dissolved in 75 ml of approximately 10% potassium hydroxide, and 8.3 g of acetic anhydride added, gradually, with mixing. After standing 30 minutes, it was acidified with dilute hydrochloric acid (1: 1). The oily precipitate which separated crystallized rapidly. The crystals were pressed out and washed with water. Yield was 11.6 g (about 97%). Melting point of the crude substance was 187-193°. After recrystallization from water, hexagonal prisms precipitated, melting at 193-194.5°.

Found %: N 5.21, 5.15. $C_{15}H_{15}O_3N$. Calculated %: N 5.45.

After acetylating 6 g of naphthylalanine by 15 minute boiling with 15 g of acetic anhydride, followed by removal of the latter by distillation in vacuo, there resulted about 7 g of a yellowish substance with m.p. 182.5-193°. Upon its recrystallization from water, 4.8 g (about 72%) of the acetyl derivative resulted with m.p. 193-194.5°, identical with the above-described, and about 0.8 g of a substance insoluble in water, with m.p. 234°. Recrystallization from glacial acetic acid did not increase the melting point. A sample mixed with the acetyl derivative produced lowering of the melting point to 185°. The substance was soluble in 1% alkali, giving a gelatinous precipitate with concentrated alkalies.

Found %: N 6.01, 5.91. Oxazine derivative $C_{15}H_{13}O_2N$. Calculated %: N 5.86.

N-Acylated naphthylalanine amides. Obtained through standard procedure by heating with thionyl chloride at 40° almost to cessation of hydrogen chloride evolution. After removal of excess $SOCl_2$ in vacuo, the residue was dissolved in dry benzene and treated by passing in dry ammonia. The separated amide was filtered off, washed with ether, 2-3% alkali hydroxide, and finally water.

β-(α-Naphthyl)-β-(N-carboethoxy)-alanine amide. The yield of purified amide from 1.5 g of the urethane, after recrystallization from alcohol, amounted to 1.0 g (66.7%).

Found %: N 9.82. $C_{16}H_{18}O_3N_2$. Calculated %: N 9.79.

β-(α-Naphthyl)-β-(N-acetyl)-alanine amide. 1.78 g of amide with m.p. 237-243° resulted from 2.5 g of β-(α-naphthyl)-β-(N-acetyl)-alanine. After recrystallization from alcohol, it precipitated in the form of long, angular needles, melting at 254-255°. The yield of purified substance was 1.5 g (about 60%).

Found %: C 70.44, 70.63; H 6.35, 6.48; N 11.17, 11.12. $C_{15}H_{16}O_2N_2$. Calculated %: C 70.27; H 6.30; N 10.94.

β-(α-Naphthyl)-β-(N-benzoyl)-alanine amide. 1.75 g (87.5%) of amide with m.p. 258-260° resulted from 2 g of β-(α-naphthyl)-β-(N-benzoyl)-alanine. The product, recrystallized from pyridine or dioxane, melted at 276.5-277°. It crystallized from dioxane in the form of needle clusters.

Found %: C 75.96, 76.09; H 5.92, 5.73; N 8.98, 8.92. $C_{20}H_{18}O_2N_2$. Calculated %: C 75.43; H 5.70; N 8.80.

2-Phenyl-4-(α-naphthyl)-6-oxotetrahydropyrimidine. Tetrahydropyrimidines are formed by heating N-benzoylated phenyl- or alkyl-alanines with thionyl chloride at 80°, with subsequent dry ammonia treatment. On carrying out this reaction with naphthyl alanine, resinification occurred and only naphthylacrylic acid amide was isolated. It was possible to obtain the corresponding 2-phenyl-4-naphthyl-6-oxotetrahydropyrimidine in low yield only under milder conditions.

For this purpose, 4.2 g of N-benzoyln a-phthylalanine, 6 g of thionyl chloride and 10 g of dry benzene were heated with gentle boiling for about 4 hours, after which the benzene and thionyl chloride excess were distilled off in vacuo. The remaining brown viscous mass was extracted with ether. With external ice cooling, the ether solution was saturated with dry ammonia and filtered off from the precipitate which separated. The latter was washed with ether and hot chloroform. The insoluble residue was washed with water and recrystallized from alcohol. There resulted about 0.7 g of N-benzoylnaphthylalanine amide with m.p. 277°, which did not give depression in melting point with pure known amide. During evaporation of the ether-chloroform solution in air, a precipitate resulted with m.p. 177-180°. After recrystallization from chloroform, the melting point increased to 187-188° and remained constant. Yield was 0.5-0.6 g (about 13%).

2-Phenyl-4-(α-naphthyl)-6-oxotetrahydropyrimidine crystallized in the form of slightly yellow platelets, readily soluble in hot chloroform, alcohol and benzene.

Found %: N 9.23, 9.22. $C_{20}H_{16}ON_2$. Calculated %: N 9.33.

A very low yield of tetrahydropyrimidine derivative resulted upon heating of the N-benzoyl-naphthylalanine amide with benzoyl chloride and acetic anhydride. The reacylation reaction was not established in the latter case.

Upon heating the N-acetyl derivative with acetic anhydride, the yield of 2-methyl-4-naphthyloxotetrahydropyrimidine amounted to 80% of theory. Silky needles (from ether). M.p. 148-149°.

Found %: N 11.32, 11.57. $C_{15}H_{14}ON_2$. Calculated %: N 11.76.

Interaction of N-benzoyl-β-(α-naphthyl)-β-alanine amide and hypobromite. 2 g of amide was introduced into a solution of hypobromite, prepared from 20 ml of 15% sodium hydroxide solution and 2.4 g of bromine at −7°, and the mixture stirred at room temperature. After 2 hours, the precipitate slowly became oily, and after another 75 minutes, a yellow viscous mass formed. Stirring was terminated and the reaction mass heated to 78-80° for 20 minutes, whereupon the resinous mass melted and then solidified again. After cooling, the precipitate was filtered off and washed with water. 0.95 g of the substance with m.p. 195-203° was isolated. After recrystallization from alcohol, there resulted 0.22 g with m.p. 221.5-222°. From the analysis and properties, this compound corresponded to naphthylglyoxalidone In mixed samples with 3-N-benzoyl-4-(α-naphthyl)-glyoxalidone, obtained according to the Curtius reaction, there was depression of melting point, but there was no depression in melting point when mixed with 4-(α-naphthyl)-glyoxalidone, obtained by saponification of acylglyoxalidone (see below).

Found %: C 73.74, 73.97; H 6.19, 6.00; N 13.41, 13.24, 13.11. $C_{13}H_{12}ON_2$. Calculated %: C 73.54; H 5.71; N 13.21.

Upon acidification of the alkaline solution, and subsequent extraction by ether, there resulted 0.77 g of the substance. The latter was distilled with steam. About 0.5 g of benzoic acid was isolated from the distillate. From its melting point and from other properties, the undistilled residue was found to be N-benzoyl-β-(α-naphthyl)-β-alanine.

At times it was possible to isolate a small amount of benzoylnaphthylglyoxalidone during the Hofmann reaction with N-benzoylnaphthylglyoxalidone amide. The difficulties in separating the acyl derivatives from the nonacylated substance is explainable by the similarity of all of the reactions and the close melting points, for preparation of the benzoylated and acetylated naphthyloxalidone of which the Curtius reaction is more applicable (see below).

Interaction of N-Acetyl-β-(α-naphthyl)-β-alanine amide and hypobromite. 2.34 g of amide was introduced into a hypobromite solution prepared from 20 ml of 15% NaOH solution and 3 g of bromine at −12°, and the mixture stirred at room temperature. After 30 minutes the amide was completely dissolved. The solution was heated. At 50° a light, white precipitate separated; at 55-60° a brown oil separated, which crystallized upon further heating. The mixture was kept for several minutes at 80°. After cooling, the precipitate was filtered off, washed with water. 1.25 g of substance with m.p. 208-215° resulted; after recrystallization from alcohol, 0.71 g with m.p. 217-220°. The resulting compound gave depression of melting point for a mixed sample with 2-N-acetyl-4-(α-naphthyl)-glyoxalidone, prepared according to the Curtius reaction, but did not give depression in mixed sample with the above-described naphthylglyoxalidone

Hofmann reaction with β-(α-naphthyl)-β-(N-carboethoxy)-alanine amide. 0.15 ml of bromine and 0.3 g of amide were added to 5 ml of 15% sodium hydroxide solution. After standing 2-3 hours (with periodic stirring) all of the amide went into solution, and a thick oil precipitated to the bottom of the flask. The reaction mass was heated to 60° and then cooled. The solid substance which precipitated out after separation from the liquid and drying, weighed 0.17 g and melted at 203-205°. After recrystallization from alcohol, the melting point rose to 221°. The product did not give depression with known pure naphthylglyoxalidone.

Ethyl ester of N-benzoyl-β-(α-naphthyl)-β-alanine. Hydrogen chloride was passed for 4 hours through a solution of 10 g of N-benzoylamino acid and 50 ml of absolute alcohol at 60-70°, and the reaction mixture then cooled to 0°, the solution saturated with hydrogen chloride and left overnight. The solvent was removed in vacuo and the residue washed with water and extracted with ether. The ether extract was washed with a weak solution of sodium bicarbonate and water, and dried over anhydrous sodium sulfate. After removal of the ether, there remained a rapidly solidifying oil. After recrystallization from alcohol, and washing with a small volume of ether, the m.p. was 109-110° (the melting point remained unchanged with a second recrystallization). Needle clusters precipitated from alcohol. Yield was 9.72 g (89.3%).

Found %: N 3.84, 3.76. $C_{22}H_{21}O_3N$. Calculated %: N 4.03.

About 0.3 g of initial N-benzoylamino acid was isolated from the wash solutions upon acidification.

Ethyl ester of N-acetyl-β-(α-naphthyl)-β-alanine. Product was obtained under the ethylating conditions of the N-benzoyl derivative. The ethyl ester of the N-aceto derivative was less soluble in ether after removal of the solvent in vacuo, and upon addition of water and ether, a copious crystalline precipitate separated. The precipitate and the ether solution were washed with a weak solution of sodium bicarbonate, and then with water.

The yield from 7.2 g of N-acetylamino acid ester was 7.3 g, or 91% of theory. M.p. was 136-139° after recrystallization from alcohol, and washing with a small volume of ether raised it to 142.5-143°. Elongated, tetraangular platelets precipitated from alcohol.

Found %: N 5.16, 4.99. $C_{17}H_{19}O_3N$. Calculated %: N 4.91.

N-benzoyl-β-(α-naphthyl)-β-alanine hydrazide. A mixture of 9.7 g of the ethyl ester of N-benzoylamino acid, 4.1 ml of hydrazine hydrate and 11 ml of absolute alcohol was heated to moderate boiling. After 15-20 minutes, a thick crystalline mass formed, to which was added 2 ml of absolute alcohol and the heating continued for another 1.5-2 hours on a water bath. After cooling, the precipitate was filtered off and washed on a filter with water, alcohol and ether. Yield was 9 g (96.6%). M.p. 254-256°, remaining unchanged by recrystallization. Elongated tetrangular platelets precipitated from the alcohol.

Found %: N 12.76, 12.69. $C_{20}H_{19}O_2N_3$. Calculated %: N 12.61.

N-Acetyl-β-(α-naphthyl)-β-alanine hydrazide. This was obtained under the conditions of N-benzoyl hydrazide derivative formtation. The yield was about 5.7 g, or 92.2% of theory, from 6.5 g of the ethyl ester of N-acetylamino acid. M.p. was 236-237°, and did not change after recrystallization from water.

Found %: N 15.49, 15.54. $C_{15}H_{17}O_2N_3$. Calculated %: N 15.5.

N-Benzoyl-β-(α-naphthyl)-β-alanine azide. 5 g of the hydrazide of N-benzoylamino acid was dissolved in 235 ml of 87-88% acetic acid, the solution cooled to 0°, and 3.6 g of finely-powdered sodium nitrite introduced in 3 to 4 portions over 15 minutes with shaking. After 5 minutes, the azide precipitated in the form of fine needles. The reaction mixture was left for 1.5 hours at 0°, and was then diluted with ice water. The azide precipitate was filtered off, washed with ice water to the disappearance of acetic acid odor, and dried in a desiccator. The yield was about 4.7 g (91%). M.p. was 83-84.5° (with decomposition).

N-Acetyl-β-(α-naphthyl)-β-alanine azide. 0.24 g of hydrazide was treated with 2.5 ml of 82% acetic acid. The mixture was cooled to 0-2°, and, with shaking, 0.31 g of finely-powdered sodium nitrite was introduced, whereupon the hydrazide dissolved completely. After 2 hours at 0°, the reaction solution was diluted with ice water. An oily product separated from the emulsion formed, which soon crystallized in the form of quadrangular prisms. The precipitate was filtered off, washed with ice water to disappearance of acetic acid odor and dried in a desiccator. Yield of azide was about 0.21 g (83%). M.p. 74-75° (with decomposition).

On carrying out the reaction in an acetate solution a substance of higher molecular weight was formed along with the azide in a series of experiments, which was separated from the azide by dissolution of the latter, with heat, in benzene. Thus, from 2.64 g of hydrazide, 0.43 g of substance with m.p. 265-270° resulted, insoluble in both acid and alkaline media. Upon heating to boiling in 2-3% sodium hydroxide solution, the melting point increased to

287-292°. The compound isolated was apparently the 1,2-di(N-acetyl-β-alanyl)hydrazine. An identical product resulted on heating the hydrazide in glacial acetic acid.

Found %: C 70.30, 70.44; H 5.97, 6.06; N 10.84, 10.92. $C_{30}H_{30}O_4N_4$. Calculated %: C 70.55; H 5.92; N 10.98.

4-(α-Naphthyl)-3-N-benzoylglyoxalidone. A solution of 4.7 g of azide in 250 ml of dry benzene was heated to boiling for 5 hours. The benzene was almost completely distilled off. After cooling, the precipitate formed was filtered off. After drying, 3.85 g of substance with m.p. 210-218° resulted. After recrystallization from alcohol, 3.05 g (about 70.7%). M.p. 222-224°, unchanged after second recrystallization. Elongated tetrangular platelets precipitated from alcohol.

Found %: N 8.57, 8.66. $C_{20}H_{16}O_2N_2$. Calculated %: N 8.86.

3-N-Acetyl-4-(α-naphthyl)-glyoxalidone. A solution of 1.75 g of N-acetyl-β-(α-naphthyl)-β-alanine azide in 75 ml of dry benzene was heated to boiling for 4 hours. After removal of benzene, 1.56 g (about 99%) of yellowish powder was left with m.p. 220-225°. After recrystallization from alcohol and benzene, m.p. 214-216°. Hexagonal prisms from alcohol precipitated.

Found %: C 71.10, 71.28; H 5.74, 5.84; N 10.66, 10.86. $C_{15}H_{14}O_2N_2$. Calculated %: C 70.83; H 5.55; N 11.02.

Saponification of 3-N-Benzoyl-4-(α-naphthyl)-glyoxalidone. 1 g of N-benzoyl-glyoxalidone was heated to moderate boiling in 50 ml of 15% NaOH solution for 5 hours. No visible changes occurred. After cooling the residue was filtered off, and washed with water. 0.74 g of substance with m.p. 185-205° resulted. Elongated tetragonal platelets precipitated from alcohol upon recrystallization, m.p. 219.5-221.5°. The yield was 0.24 g. In addition, through partial evaporation of the mother liquor, there was obtained another 0.12 g of substance with m.p. 215-219°; thus the total yield constituted 53.6% of theory. Mixed samples of the compound derived from the initial benzoyl derivative gave a depression in melting point, which did not occur when it was mixed with 4-(α-naphthyl)-glyoxalidone, obtained according to the Hofmann method. At the same time benzoic acid in about 78% of theory was isolated.

Saponification of 3-N-acetyl-4-(α-naphthyl)-glyoxalidone. 0.5 g of 3-N-acetyl-4-(α-naphthyl)-glyoxalidone was heated to gentle boiling in 25 ml of 15% sodium hydroxide solution for 5 hours. After cooling, the precipitate was filtered off and washed with water. 0.4 g of substance resulted (95.8% of theory), with m.p. 220-222°. After recrystallization from alcohol, elongated tetragonal platelets precipitated. M.p. was 221-222°. A mixed sample of the product with initial N-acetylnaphthylglyoxalidone gave a depression in melting point, which did not occur when mixed with 4-(α-naphthyl)-glyoxalidone.

SUMMARY

1. Synthesis of β-(α-naphthyl)-β-ureidopropionic acid has been carried out by two procedures: heating of β-(α-naphthyl)-β-alanine with urea, and heating of N-carboethoxynaphthylalanine with dilute alkali.

2. It has been determined that in the usual synthesis of 2-phenyl-4-aryl(alkyl)-6-oxotetrahydropyrimidine (heating of N-benzoylated-β-alkyl (aryl)-β-alanines with thionyl chloride and subsequent treatment with dry ammonia), N-benzoyl-β-(α-naphthyl)-β-alanine does not give ring closure, and upon desamination, forms α-naphthylacrylic acid amide.

3. It has been found that desired phenylnaphthylpyrimidine can be obtained in low yield by treating N-benzoylnaphthylalanine with thionyl chloride under milder conditions (heating in benzene medium). The same compound can be obtained by interacting N-benzoylnaphthylalanine with benzoyl chloride or acetic anhydride.

4. Conversion of β-(α-naphthyl)-β-alanine to naphthylglyoxalidone has been accomplished by both the Hofmann reaction (interacting the amides of acylated naphthylalanines with alkaline hypobromite) and according to the Curtius reaction (boiling the acylated naphthylalanine azides in benzene solution). In the latter case, acylated α-naphthylglyoxalidones are formed in high yield.

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* See Consultants Bureau Translation, page 847.

** " " " " 231.

HOFMANN REACTION WITH α-BROMOSUBSTITUTED ACID AMIDES

V. M. Rodionov, E. N. Alekseeva and V. A. Vaver

In 1905 N. M. Kizhner [1] for the first time used the Hofmann reaction on α-bromosubstituted acid amides for the synthesis of cyclobutanone from α-bromocyclobutancarboxylic acid, and made the assumption that this reaction course with amides of the aliphatic α-bromosubstituted acid should lead to formation of aldehyde or ketone, depending upon structure of the acid.

He confirmed this assumption by synthesizing acetone from α-bromosubstituted acid amide. In 1908 [2] Mossler made an observation that when α-bromosubstituted acid amides are heated with alkali, rupture of HCN proceeds, with formation of aldehydes; however, Mossler did not isolate the aldehydes and did not carry out their quantitative determination, but instead, made his deductions on the basis of qualitative reactions and quantitative determination of HCN. In 1934 Brown [3] obtained aldehydes from α-bromosubstituted acid amides, utilizing the Curtius reaction.

In the present work the Hofmann reaction was carried out with α-bromoisovaleric, α-chlorocaproic, α-bromoenanthic, α-bromoundecyclic, α-bromodiethylacetic and α,α'-dibromoadipic acid amides. Reaction was carried out in both hypobromite solution and in sodium hypochlorite solution. The best yields of aldehydes resulted by treatment of α-bromosubstituted amides with alkaline hypochlorite solution, and immediate removal of the forming aldehyde from the sphere of reaction. Aldehyde yield depends upon its boiling point. The best yield (65-69% of theory) is obtained with the lowest boiling, isobutyric aldehyde; N-capric aldehyde resulted in 23% yield of theory.

To clarify the question of how the nature of the halogen affects the reaction course, experiments were set up with α-chlorocaproic acid amide. Replacement of bromine by chlorine did not increase aldehyde yield. All experiments with the monobasic acid amides, with exception of diethylacetic acid amide, were accompanied by considerable resin formation. The amount of resin increased with increase in boiling point of the resulting aldehyde. Reaction with α-bromodiethylacetic acid amide proceeded with extensive destruction of the molecule, and instead of diethylketone, the aldehyde was obtained. Diethylketone formed only in that case where reaction was carried out with large excess of alkali. α,α'-Dibromoadipic acid diamide under conditions of the Hofmann reaction, produced neither aldehyde nor resin. There was isolated fromthe reaction mixture succinic acid in the amount 10-11% of the amide taken.

In experiments arranged for the purpose of synthesizing urethanes both under normal conditions and in sealed tubes, the initial α-bromosubstituted amide resulted quantitatively in all cases.

EXPERIMENTAL

Hofmann Reaction with α-Bromoisovaleric Acid Amide

α-Bromoisovaleric acid was obtained in 80% yield according to the method proposed for α-bromocaproic acid [4]. On reaction with PCl_3, the acid was converted into chloroanhydride, which, with vigorous mechanical stirring, was then added slowly to 33% ammonia solution cooled to −5°.

4.5 g of amide (0.025 mole) with m.p. 132° was introduced in small portions with mechanical stirring into the hypobromite solution obtained at −5° from 4 g of NaOH (0.1 mole), 35 ml of water and 1.28 ml (0.025 mole) of bromine. The last portion of amide, while dissolving, caused decolorization of the solution. The slightly turbid, colorless solution was transferred to a flask for steam distillation, and was heated with a stream of steam as rapidly as possible. The solution immediately became turbid and foamy at 50-70°, the aldehyde distilling off rapidly with the steam. The ammonia which distilled off along with the aldehyde was duly neutralized with hydrochloric acid; 35 ml of 4% $NH_2OH \cdot HCl$ in 60% alcohol was added to the solution. After a half-hour the hydrochloride which separated was titrated with 0.6835 N KOH: vol. = 15.38 ml; aldehyde found − 0.757 g (42%).

Reaction with Sodium Hypochlorite

The hypochlorite was prepared by passing a current of chlorine at −5° into 8 g of NaOH (0.2 mole) in 70 ml of water until the weight increase reached 3.6 g (0.05 mole). 9 g (0.05 mole) of α-bromoisovaleric acid amide was introduced into the resulting solution with mechanical stirring, after which the reaction mixture was distilled with steam. The receiver was immersed in cooling mixture. The resulting distillate was distilled a second time; the second distillate was salted out with sodium chloride. The aldehyde was separated, dried and distilled. 2.26 g (63%) resulted, b.p. 64-66°. Melting point of the 2,4-dinitrophenylhydrazone was 181.5°.

Reaction with α-Bromoenanthic Acid Amide

α-Bromoenanthic acid amide was prepared in the same manner as the α-bromoisovaleric acid amide. White crystals, readily soluble in a majority of organic solvents, insoluble in cold and poorly soluble in hot water. M.p. 58° (from ligroin).

Found %: N 6.84; Br 38.61. $C_7H_{14}ONBr$. Calculated %: N 6.73; Br 38.46.

5 g (0.025 mole) of α-bromoenanthic acid amide was added to the sodium hypochlorite solution prepared as in the preceding experiment. The cooled amide solution was added to the hypochlorite solution in the flask by a dropping funnel, the flask being set up for steam distillation, heated on a boiling water bath; superheated steam was passed through the flask. The aldehyde distilled off with steam was extracted with ether. After drying with sodium sulfate, and distilling off the ether, 1.4 g (56%) of caproic aldehyde with b.p. 128-131° resulted. Melting point of the 2,4-dinitrophenylhydrazone was 104°.

Found %: N 19.96, 19.89. $C_{12}H_{16}O_4N_4$. Calculated %: N 20.00.

Reaction with α-Bromoundecylic Acid Amide

α-Bromoundecylic acid amide was synthesized from undecylic acid by the same procedure as with the preceding amides, with 70% yield, calculating on the basis of chloroanhydride. White crystals, insoluble in both cold and hot water, soluble in hot methanol. M.p. 59° (after two recrystallizations from methanol).

Found %: N 5.76; Br 30.55, 30.31. $C_{11}H_{22}ONBr$. Calculated %: N 5.30; Br 30.30.

9.9 g of α-bromoundecylic acid amide (0.0375 mole) was dissolved in 50 ml of methanol and was added, with mechanical stirring, to the sodium hypochlorite solution obtained at −5° from 60 ml of water, 6 g (0.15 mole) of sodium hydroxide and 2.7 g (0.0375 mole) of chlorine. At first a thin suspension precipitated, which then dissolved rapidly, forming a transparent colorless solution. The cooled reaction mixture was added dropwise to the flask for steam distillation which was internally heated by a current of superheated steam, with simultaneous external heating. The distillate was extracted repeatedly with ether. After distilling off the ether, 1.8 g of the substance with b.p. 203-205° resulted. Melting point of 2,4-dinitrophenylhydrazone was 102°.

Reaction with α-Chlorocaproic Acid Amide

α-Chlorocaproic acid was obtained by chlorination of N-butylmalonic ester. 120 g (0.47 mole) of N-butylmalonic ester was placed in a three-necked flask equipped with stirrer, reflux condenser and bubbler for chlorine supply. The reaction mass was heated to 80° and a strong current of chlorine gas was passed through the liquid with vigorous stirring. Completion of reaction was determined by increased weight of absorbed chlorine. The calculated weight increase was 20 g, resulting weight increase was 22 g. 123 g of chlorobutylmalonic ester with b.p. 134-138° at 8 mm resulted.

To obtain the α-chlorocaproic acid, the ester was cooled to −10° and was mixed with 56 g of KOH in 500 ml of absolute alcohol solution precooled to −5°. After several minutes, the mixture solidified to a uniform white mass which was kept for 6 hours in a cooling mixture. The dipotassium salt of α-chloro-N-butylmalonic acid was filtered with suction, washed with small quantities of ether and dissolved in 200 ml of water. The solution was cooled to 0°, acidified with cooled dilute sulfuric acid to an acid reaction with Congo red, and extracted with ether. The ether extract was dried with sodium sulfate. After distilling off the ether, decarboxylation of N-butyl-α-chloromalonic acid was carried out by slow distillation in vacuo from a flask with dephlegmator. There resulted 33 g with b.p. 120-122° at 10 mm.

To synthesize α-chlorocaproic acid chloroanhydride, 21 g (0.15 mole) of phosphorus trichloride was added to the obtained preparation over a period of 2 hours at 80-85°, and the reaction mixture then kept for 4 hours at 100-105° to the cessation of HCl evolution. The α-chlorocaproic acid chloroanhydride was used without further purification for synthesis of the amide. The amide resulted in 61% yield of theory according to the above-described procedure. Lustrous white leaflets, m.p. 61° (from water).

Found %: N 9.41, 9.29; Cl 23.29, 23.35. $C_6H_{12}ONCl$. Calculated %: N 9.36; Cl 23.74.

The Hofmann reaction was carried out under the same conditions as for α-bromoenanthic acid amide. n-Valeric aldehyde resulted in 65.5% yield of theory. B.p. 100-102°. Melting point of the dinitrophenylhydrazone was 98°.

Reaction with α-Bromoundecylic Acid Amide

α-Bromoundecylic acid resulted in 57.5% yield of theory on reacting dry bromine with undecylic acid in the presence of 1 ml of phosphorus trichloride. B.p. 156-165° at 4 mm. The chloroanhydride was obtained by addition of PCl_3 at 85-90°, with subsequent holding at 110-115° for 4-5 hours. Yield was 64% of theory, b.p. 130-136° at 6 mm.

The amide was synthesized under the above-described conditions; yield 70%. White crystals insoluble in both cold and hot water, soluble in methanol. After two crystallizations from methanol, the m.p. was 59°.

Found %: N 5.76; Br 30.31, 30.55. $C_{11}H_{22}ONBr$. Calculated %: N 5.31; Br 30.30.

The amide was insoluble in hypochlorite, and therefore, to carry out the experiment it was first dissolved in methanol, and the resulting solution then added to hypochlorite. The Hofmann reaction was carried out under the same conditions as in the preceding experiments. For isolation of the aldehyde, the reaction mixture was added from a dropping funnel to the flask which was heated from within by superheated steam, and at the same time from without. Yield was 23% of theory. Melting point of the dinitrophenylhydrazone was 102°.

Reaction with α-Bromodiethylacetic Acid Amide

Reaction was carried out with α-bromodiethylacetic acid amide under the same conditions as for the other acids, and was accompanied by extensive decomposition of the substance. The distillate gave qualitative reactions for aldehyde.

7.35 g (0.038 mole) of α-bromodiethylacetic acid amide were dissolved in sodium hypochlorite prepared from 7.3 g (0.182 mole) of NaOH, 73 ml of water and 2.7 g (0.038 mole) of chlorine (4.8 mole alkali per 1 mole of amide and 1 mole of chlorine). Steam was passed through the resulting solution. The distillate was extracted with ether. 0.8 g (25%) of the substance with b.p. 101° resulted. Melting point of the dinitrophenylhydrazone of diethylketone was 155.5°.

Found %: N 21.26, 21.10. $C_{11}H_{14}O_4N_4$. Calculated %: N 21.05.

Reaction with α,α'-Dibromoadipic Acid Diamide

α,α'-Dibromoadipic acid diamide was obtained by reacting 25% ammonia solution with the diethyl ester of α,α'-dibromoadipic acid. Yield was 60-65%. The amide was insoluble in cold water, and hydrolyzed readily upon boiling with water; very poorly soluble in all organic solvents. Lustrous white needles. After recrystallization from benzene, m.p. was 183° with decomposition.

Found %: C 23.61, 23.65; H 3.28, 3.18; N 9.01, 8.99; Br 53.12, 52.81. $C_6H_{10}O_2N_2Br_2$. Calculated %: C 23.84; H 3.31; N 9.27; Br 52.98.

15 g (0.05 mole) of α,α'-dibromoadipic acid diamide was dissolved in hypochlorite prepared from 140 ml of water, 16 g of NaOH and 7.2 g of chlorine. The transparent, almost colorless, solution was added to the flask by means of a dropping funnel, through which flask a stream of superheated steam was passed. The flask for steam distillation was placed in a boiling water bath. During the entire distillation, the solution in the flask remained transparent, no resin forming. Qualitative test for aldehyde in the distillate was negative. The amount of ammonia in the distillate constituted 65% of theory. The solution left after steam distillation was evaporated to 150 ml, cooled to 0°, acidified with dilute H_2SO_4 to an acid reaction with Congo red. The separated bromine was tied up by addition of a small amount of concentrated $NaHSO_3$ solution. The solution was extracted with ether, the ether extract dried with sodium sulfate. After distilling off the ether, 0.6 g of crystalline substance remained, which was pressed out onto a porous plate, and washed with dry ether. M.p. 187-188°. The sample mixed with pure succinic acid did not give a depression in melting point.

SUMMARY

The Hofmann reaction has been carried out with amides of α-bromoisovaleric, α-chlorocaproic, α-bromoenanthic, α-bromoundecylic, α-bromodiethylacetic and α,α'-dibromoadipic acids.

The best yields of aldehydes result when α-bromosubstituted amides are treated with an alkaline solution of hypochlorite with immediate removal of the forming aldehyde from zone of reaction.

Replacement of bromine by chlorine does not increase aldehyde yields.

During reaction of α-bromodiethylacetic acid amide, aldehyde is formed instead of diethyl ketone. Diethylketone results in that case where reaction is carried out with large excess of alkali.

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SYNTHESIS OF 2-MERCAPTO-IMIDAZOLYL-PROPIONIC ACID

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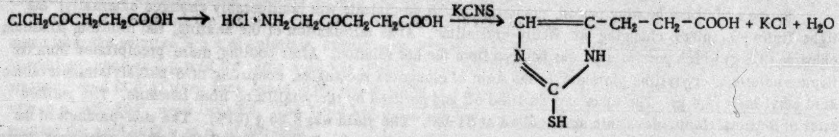
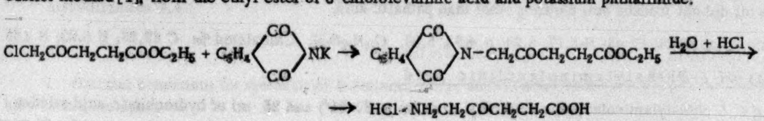
It follows from the literature that synthesis of many imidazole derivatives is a rather complex problem.

In studying various procedures for synthesis of these compounds, it was found that it is possible to obtain, in very good yields, 2-mercapto-imidazolyl-propionic acid, and related compounds, from δ-chlorolevulinic acid, according to the following scheme:


ClCH₂COCH₂CH₂COOH → HCl·NH₂CH₂COCH₂CH₂COOH
KCNS
CH=C–CH₂–CH₂–COOH + KCl + H₂O
N
NH
C
SH

The first stage of this synthesis is the preparation of δ-aminolevulinic acid hydrochloride, according to the Gabriel method [1], from the ethyl ester of δ-chlorolevulinic acid and potassium phthalimide:



By hydrolyzing the ethyl ester of δ-phthalylaminolevulinic acid, as with the work of Rodionov and Yartseva [2], it was also possible to isolate an intermediate hydrolysis product – δ-phthalylaminolevulinic acid.

Condensation of the ethyl ester of δ-chlorolevulinic acid and potassium phthalimide was carried out in absolute alcohol, the reaction mixture being boiled on a water bath. The reaction products were found, on one hand, to be the ethyl ester of δ-phthalylaminolevulinic acid and potassium chloride, and on the other – phthalimide and a highly resinified viscous oil, whose composition and structure were not investigated.

After removal of potassium chloride from the hot reaction mixture by filtration, there precipitated from the filtrate upon cooling colorless, crystalline platelets of δ-phthalylaminolevulinic acid ethyl ester, with m.p. 81-82°. Yield was 51% of theory. Analytical data for nitrogen, carbon and hydrogen corresponded completely to those calculated according to the formula $C_{15}H_{15}O_5N$. The ethyl ester of δ-phthalylaminolevulinic acid is not described in the literature, and has been synthesized for the first time.

Upon hydrolysis of the resulting ester, two new compounds were isolated which have not been described in the literature: the hydrochloride of δ-aminolevulinic acid and δ-phthalylaminolevulinic acid.

The hydrochloride of δ-aminolevulinic acid resulted on boiling the ethyl ester of δ-aminolevulinic acid in a dilute solution of hydrochloric acid (1:1). The hydrochloride crystals separated from reaction solution after removal of the phthalic acid, and the filtrate, decolorized by charcoal, was evaporated to as small a volume as possible. Melting point of the pure hydrochloride was 150-151°. Yield was 93%. Analytical data for chlorine and nitrogen corresponded to that calculated according to the formula $C_5H_{10}O_3NCl$.

δ-Phthalylaminolevulinic acid was obtained by hydrolysis of the ethyl ester by heating to complete dissolution in a dilute solution of hydrochloric acid (1:3). A colorless, fluffy precipitate, composed of small crystalline needles, separated out from the reaction mixture upon cooling, with m.p. 159°. The yield was 85% of theory. Analytical data for nitrogen corresponded to the formula $C_{13}H_{11}O_5N$. In addition, 2-mercapto-imidazolyl-propionic acid, described for the first time by Akabori [4], was synthesized from δ-aminolevulinic acid hydrochloride and potassium thiocyanate according to the Wohl and Marckwald method [3]. 2-Mercapto-imidazolyl-propionic acid represented colorless, crystalline needles, soluble in water with heating, and readily soluble in alcohol and acetic acid; after repeated recrystallizations, the m.p. was 207-208°. Yield was 72.7% of theoretical amount.

Analytical data for nitrogen and for water of crystallization coincided well with the calculated, according to the formula $C_6H_8O_2N_2S \cdot H_2O$.

2-Mercapto-imidazolyl-propionic acid was obtained for the first time from the hydrochloride of aldehydo-glutamic acid and potassium thiocyanate in 40% yield; m.p. was 205-206.5°.

EXPERIMENTAL

Synthesis of the Ethyl Ester of δ-Phthalylaminolevulinic Acid

10 g of the ethyl ester of δ-chlorolevulinic acid in 60 ml of absolute ethyl alcohol and 10.1 g of potassium phthalimide were introduced into a flask equipped with reflux condenser and a calcium chloride tube. The mixture was heated on a water bath for 5 hours, moderate boiling being maintainedin the flask.

By the end of the heating period, the nature of the precipitate was considerably changed externally: the light, fluffy precipitate changing into finely-crystalline. After termination of the heating, the resulting potassium chloride (3.6 g) which precipitated was filtered from the hot solution. After cooling, there precipitated from the filtrate colorless, crystalline platelets, in the form of elongated rectangles, consisting of δ-phthalylaminolevulinic acid ethyl ester (9.4 g). The ether was distilled off and purified by recrystallizing from benzene. The purified ester of δ-phthalylaminolevulinic acid melted at 81-82°. The yield was 8.25 g (51%). The side-products of the reaction were found to be phthalimide (2.5 g) and an oil (5.25 g) of unknown composition, which gave upon storage additional quantities of δ-phthalylaminolevulinic acid ethyl ester, phthalimide and potassium chloride. Saponification of the oil did not produce new products other than phthalic acid.

Found %: C 62.24, 62.48; H 5.17, 5.20; N 4.93, 5.08. $C_{15}H_{15}O_5N$. Calculated %: C 62.26; H 5.23; N 4.85.

Synthesis of δ-Phthalylaminolevulinic Acid

2.9 g of δ-phthalylaminolevulinic acid ethyl ester (m.p. 80-81°) and 25 ml of hydrochloric acid solution (1:3) were placed in a flask equipped with reflux condenser. The mixture was heated on a wire gauze for 20 minutes, whereupon the ester dissolved and the oil dissolved by saponification. Following this, heating was terminated. There was observed upon cooling copious separation of loose, light precipitate in the form of needle crystals.

δ-Phthalylaminolevulinic acid was readily soluble in alcohol, in water with heating, and poorly soluble in ether. After recrystallization from alcohol, the m.p. was 159°. Yield was 85% of theory.

Found %: N 5.62, 5.61. $C_{13}H_{11}O_5N$. Calculated %: N 5.37.

Semicarbazone of δ-Phthalylaminolevulinic Acid

0.52 g of δ-phthalylaminolevulinic acid was dissolved in 2 ml of alcohol diluted with 2 ml of water; 0.6 ml of the semicarbazide solution, prepared according to Zelinsky [5], was added to the resulting solution. Soon after pouring in the solution, crystals of δ-phthalylaminolevulinic acid semicarbazone precipitated out, insoluble in water, poorly soluble in alcohol. After recrystallization from alcohol, the m.p. was 202-203°, with decomposition, yield 97%.

Found %: N 17.73; 17.90. $C_{14}H_{14}O_5N_4$. Calculated %: N 17.61.

Synthesis of δ-Aminolevulinic Acid Hydrochloride

6 g of δ-phthalylaminolevulinic acid ethyl ester (m.p. 80-81°) and 90 ml of hydrochloric acid solution (1:1) were introduced into a flask equipped with reflux condenser and gas outlet tube terminating over water. The reaction mixture was heated on a wire gauze to gentle boiling for 6 hours, and then left overnight. On the following day 3.4 g of phthalic acid (m.p. 200-202°) was filtered off. The filtrate was evaporated to one-half volume, boiled with activated charcoal, and again evaporated to the point of crystalline film formation on the surface of the solution. Upon cooling of the filtrate, 2.45 g of colorless crystals separated, which melted at 150-151°. In addition, there was recovered from the motner liquor after evaporation, 0.8 g of the hydrochloride (m.p. 145-147°). The total yield of hydrochloride was 3.25 g (93%).

Found %: N 8.62, 8.65; Cl 21.19. $C_5H_{10}O_3NCl$. Calculated %: N 8.36; Cl 21.16.

Semicarbazone of δ-Aminolevulinic Acid Hydrochloride

1 g of the hydrochloride of δ-aminolevulinic acid was dissolved in 3 ml of 50% methyl alcohol, and to the

resulting solution was added 2 ml of the semicarbazide mixture, prepared according to Zelinsky [5]. Copious separation of crystals proceeded very rapidly. The semicarbazone obtained was poorly soluble in alcohol, readily so in water with heating. Yield was 1.2 g (90%). The semicarbazone, recrystallized from methyl alcohol, melted at 204.5° with decomposition.

Found %: N 25.28; Cl 15.91, 15.96. $C_6H_{13}O_3N_4Cl$. Calculated %: N 24.95; Cl 15.79.

Synthesis of 2-Mercapto-imidazolyl-propionic Acid

4 g of δ-aminolevulinic acid hydrochloride was dissolved in 50 ml of water, and 5 g of potassium thiocyanate in 10 ml of water; the solutions were mixed and left overnight at room temperature.

On the following day, the reaction mixture was evaporated on a water bath until a crystalline film appeared on the surface of the solution, whereupon it was then cooled and the colorless crystals of 2-mercapto-imidazolyl-propionic acid which precipitated then filtered off. The resulting acid was liberated by separation of potassium chloride from its solution in hot absolute alcohol (35-45 ml). The mineral salt was filtered off, and solvent distilled off from the filtrate, and the resulting crystalline residue again dissolved in water (25 ml) with heating. There resulted from the solution 3.3 g of colorless, needle-like crystals of 2-mercapto-imidazolyl-propionic acid monohydrate. In addition, another 0.5 g of the same acid was isolated from the mother liquor. The crystals of 2-mercapto-imidazolyl-propionic acid (3.8 g) were once again dissolved in water (7.5 ml) with heat, and upon cooling, colorless crystals, with m.p. 202-204°, were isolated. The yield was 3.3 g (72.7%). After repeated recrystallizations from water, there resulted the acid with a m.p. of 207-208°.

Found %: N 14.27; water of crystallization 9.30, 9.37. $C_6H_8O_2N_2S \cdot H_2O$. Calculated %: N 14.74; water of crystallization 9.47.

SUMMARY

1. Optimal conditions for synthesis of δ-aminolevulinic acid hydrochloride, not described in the literature, have been developed.

2. A new method for synthesis of 2-mercapto-imidazolyl-propionic acid, in almost double the yield as compared with the literature data, has been found.

3. δ-Phthalylaminolevulinic acid ethyl ester, δ-phthalylaminolevulinic acid, and the semicarbazones of δ-aminolevulinic acid hydrochloride and δ-phthalylaminolevulinic acid have been prepared in good yields.

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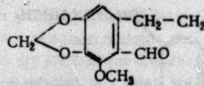
THE CHARACTERIZATION OF COTARNINE, HYDRASTININE, THEIR BENZOYL DERIVATIVES, AND INTERACTION OF COTARNONE WITH MALONIC ACID AND AMMONIA

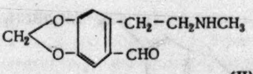
V. M. Rodionov and M. G. Chentsova

It has been demonstrated many times that cotarnine (I) and hydrastinine (II) can react in three tautomeric forms, one of which is found to be the aldehyde form.



(I)

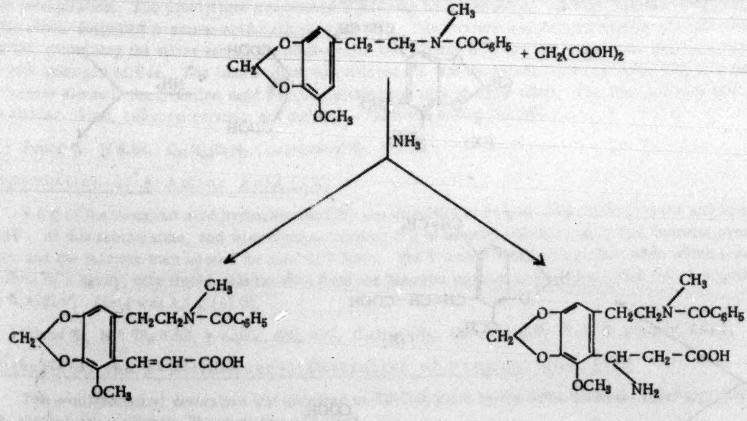
and



(II)

The presence of an aldehyde group is confirmed by the many characteristic reactions of these compounds, for example, of dismutation [1], of condensation with substances containing active hydrogen such as acetone, nitromethane, malonic ester [2], and so forth.

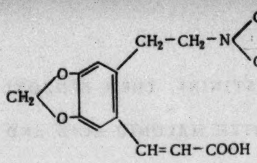
The feasibility of such a structure for cotarnine and for hydrastinine prompted an investigation of their condensation reactions with malonic acid in the presence of ammonia, according to the method of Rodionov [3], in order to obtain new complex β-amino acids. The reaction was carried out with cotarnine and its derivatives, benzoylcotarnine and cotarnone, as well as with benzoylhydrastinine. It was found, under normal conditions of synthesis, that the main reaction product is an unsaturated acid; the yield of β-amino acid was relatively small. Upon condensing with benzoylcotarnine, an unsaturated acid (III) resulted in 68% yield, calculated for benzoylcotarnine, and the β-amino acid (IV) in 15-15.5% yield.



(III) (IV)

To characterize the β-amino acid (IV), its benzoyl and p-nitrobenzoyl derivatives were prepared. The unsaturated acid (III) was converted into the ester, and its dibromo- and monobromo- derivatives were obtained as well. This acid was apparently synthesized at an earlier date by Ahlers, but was not isolated in chemically pure form [4].

Under the same conditions of condensation, benzoylhydrastinine gave about 64% of an unsaturated acid (V) and 22% of β-amino acid (VI):



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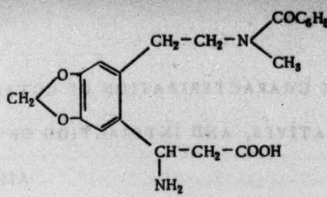
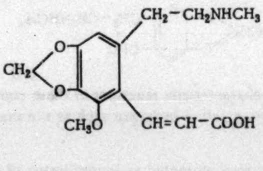


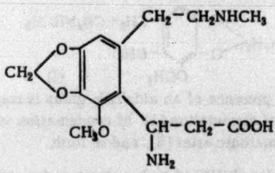
(VI)

The unsaturated character of the acid (V) was confirmed by its conversion into the dibromo derivative.

Reaction of malonic acid and ammonia with cotarnine resulted in a mixture of two amino acids (VII) and (VIII), difficult to separate, from which it was possible to isolate only the unsaturated amino acid (VII) in chemically pure form:



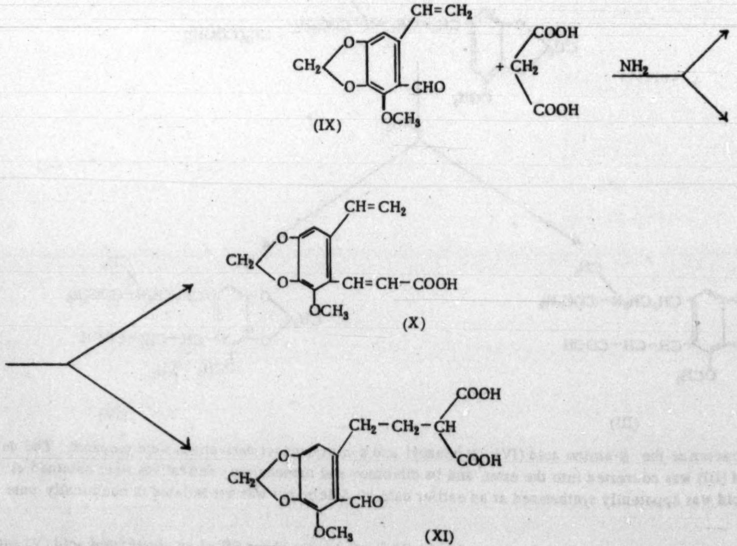
(VII)



(VIII)

The acetyl derivative of the unsaturated acid (VII) was obtained earlier by Bouman [2], by condensation of cotarnine with acetic anhydride; the unsaturated acid, its ethyl ester, as well as the dibromo derivative, are described by E. A. Postovskaya.

During synthesis of the cotarnine derivative, cotarnone (IX), there were isolated two unsaturated acids — a monobasic (X) and apparently a dibasic (XI); no amino acid was found.



For determination of the unsaturated acid structure (X), it was converted into the tetrabromo derivative.

EXPERIMENTAL

Condensation of Benzoylcotarnine With Malonic Acid and Ammonia

30 g of benzoylcotarnine, 50 g of 11% ammonia solution in absolute ether and 10 g of malonic acid were heated on a water bath in a flask with upright condenser for 3.5-4 hours. The bath temperature was slowly raised in order to distill off the alcohol and ammonia gradually, and the bath was heated to boiling only during the last hour. After termination of the heating, the residue in the flask, representing a brown, vitreous mass, was dissolved in a small excess of 5% soda solution, which was separated from suspended impurities by filtration, and precipitated by hydrochloric acid. A precipitate of the unsaturated acid (III) formed, a viscous, light-yellow, poorly crystallizing mass. Weight of the air-dried product was 23 g (about 68%).

~~The acid was~~ readily soluble in alcohol and acetic acid, poorly so in benzene, chloroform, and very poorly in water. It decolorized bromine water and permanganate solution. After three recrystallizations from 50% acetic acid, m.p. was 132-133°.

Found %: N 3.79; g-equiv. 377.1, 381.7. $C_{21}H_{21}O_8N$. Calculated %: N 3.65; g-equiv. 383.2.

The solution separated from the precipitate of unsaturated acid, containing the hydrochloride of β-amino acid (IV), as well as excess malonic acid and a small amount of unsaturated acid, was evaporated to dryness on a water bath. The dry residue was dissolved in absolute alcohol to separate mineral salts, and again evaporated to dryness, followed by solution in a small volume of water to remove traces of unsaturated acid, and after another evaporation, was dissolved in as small an amount of absolute alcohol as possible.

The β-amino acid hydrochloride was then isolated by precipitation with absolute ether in the form of a viscous mass, converting into white crystals upon repeated washings with ether in the porcelain funnel.

After drying over phosphorus pentoxide, it melted at 115° (with decomposition). The yield was 6 g, 15.6% relative to benzoylcotarnine. A highly hygroscopic substance, very soluble in water and alcohol.

Found %: N 6.72; Cl 8.51, 8.23. $C_{21}H_{25}O_8N_2Cl$. Calculated %: N 6 41; Cl 8.13.

Isolation of β-Amino Acid (IV) From the Hydrochloride

A solution of sodium hydroxide was added to an aqueous solution of 4 g of silver nitrate to the point of complete precipitation. The precipitate was washed repeatedly by decantation, and then mixed with a solution of 1.3 g of the above-described β-amino acid hydrochloride (IV). The mixture was warmed slightly and left overnight. The solution, containing the silver salt of the amino acid, was filtered off from the precipitate, and the silver precipitated with hydrogen sulfide. The liquid which was filtered off, was evaporated and after dissolving in a small volume of absolute alcohol, the β-amino acid was precipitated out with absolute ether. The acid was very soluble in water and alcohol. Fine, colorless crystals, not melting. Yield was 0.85 g (71.0%).

Found %: N 6.94. $C_{21}H_{24}O_8N_2$. Calculated %: N 7.00.

Benzoylation of β-Amino Acid (IV)

4.5 g of the β-amino acid hydrochloride (IV) was dissolved in 54 g of 10% NaOH solution and heated to 40-45°. At this temperature, and with vigorous stirring, 8 g of benzoyl chloride was added dropwise over 1-1.5 hours, and the mixture then heated for another 2 hours. The β-amino acid benzoyl derivative which separated in the form of a heavy, oily liquid, was isolated from the reaction mixture and recrystallized from benzene. M.p. was 213-214°. Yield was 3.1 g (61%).

Found %: N 5.78, 5.86; g-equiv. 492, 496. $C_{28}H_{28}O_7N_2$. Calculated %: N 5.55; g-equiv. 504.2.

Synthesis of the p-Nitrobenzoyl Derivative of β-Amino Acid (IV)

The p-nitrobenzoyl derivative was prepared in 70-71% yield by the same method. After recrystallization from alcohol-ether mixture, the m.p. was 212-214°.

Found %: N 7.96. $C_{28}H_{27}O_9N_3$. Calculated %: N 7.65.

Bromination of the Unsaturated Acid (III)

Bromine solution in acetic acid was added dropwise to a solution of 10 g of unsaturated acid (III) in 30 ml of glacial acetic acid until bromine decolorization ceased. Reaction was carried out with ice cooling. After standing for 42 hours, the mixture was poured into 500 ml of water, whereupon the dibromo derivative of the unsaturated acid (III) immediately precipitated out as a solid. After crystallization from benzene, ether or acetic acid, the m.p. was 181-183° (with decomposition). It was not possible to determine the equivalent weight of this acid by titration with alcoholic sodium hydroxide since HBr splits off.

Found %: Br 28.98, 28.99. $C_{21}H_{21}O_6NBr_2$. Calculated %: Br 29.48.

HBr Split Fromthe Dibromoderivative of the Unsaturated Acid (III)

A solution of 1 g of 2-β-(N-methyl-N-benzoyl)-aminoethyl-4,5-methylendihydroxy-6-methoxy-β-phenyl-α,β-dibromopropionic acid in 5 ml of ethyl alcohol was placed in a flask equippped with reflux condenser and heated with 0.3 g of NaOH solution in 2 ml of water on a water bath at 90° for 1 hour. Upon cooling, a copious precipitate of 2-β-(N-methyl-N-benzoyl)-aminoethyl-4,5-methylendihydroxy-6-methoxymonobromocinnamic acid sodium salt separated in the amount of 0.5 g. A solution of the salt slowly decolorized bromine water and potassium permanganate.

Found %: Br 15.56, 15.60. $C_{21}H_{19}O_6NBrNa$. Calculated %: Br 16.56.

Synthesis of Unsaturated Acid (III) Ethyl Ester

An aqueous solution of silver nitrate was added to a solution of 6 g of the unsaturated acid (III) in ethyl alcohol. The resulting precipitate of silver salt was filtered off, washed several times with water and alcohol, and dried over calcium chloride in a desiccator protected from light. The dry residue of silver salt was mixed with 10 g of ethyl bromide and 20 g of absolute alcohol in a flask equipped with reflux condenser, and was heated on a water bath to boiling for 2 hours. A heavy precipitate of silver bromide resulted. The precipitate was filtered off and the excess ethyl bromide plus some of the alcohol were distilled off from the filtrate. After cooling, the residue formed a thick mush of crystals of the ethyl ester of the unsaturated acid (III). The crystals were pressed out on a porous plate, dried, and then washed with a small volume of ether. M.p. was 106-109°. Yield was 4.2 g (65%).

To purify from unsaturated acid, the residue was dissolved in ether and the ether layer washed with 15% soda. After partial removal of solvent, the ester separated in the form of colorless, flaky crystals, with m.p. 109-110°.

Found %: N 3.72, 3.89. $C_{23}H_{25}O_6N$. Calculated %: N 3.40.

Condensation of Benzoylhydrastinine with Malonic Acid

Condensation and isolation of the reaction products were carried out in the same manner as with the above-described method for benzoylcotamine. From 4.8 g of benzoylhydrastinine, there were obtained 3.2 g (60%) of unsaturated acid (V) and 1.2 g (22%) of β-amino acid hydrochloride (VI).

The unsaturated acid, recrystallized from alcohol, melted at 177°; it decolorized bromine water and potassium permanganate solution.

Found: g-equiv. 357.6, 354.2. $C_{20}H_{19}O_5N$. Calculated: g-equiv. 353.

β-Amino acid hydrochloride melted at 140° (with decomposition).

Found %: N 7.19, 7.14. $C_{20}H_{23}O_5N_2Cl$. Calculated %: N 6.89.

Bromination was carried out under the same conditions as with bromination of the unsaturated acid (III).

The dibromo derivative, 2-β-(N-methyl-N-benzoyl)-aminoethyl-4,5-methylendihydroxy-β-phenyl-α,β-dibromopropionic acid, separated in the form of a viscous mass, crystallizing upon standing for several days. It crystallized from benzene or acetic acid. M.p. was 158-160° (with decomposition). It dissolved readily in alcohol and ether, very poorly in water.

Attempt to titrate with an alcoholic sodium hydroxide solution did not yield an equivalent point since it split off HBr.

Found %: Br 30.59, 30.55. $C_{20}H_{19}O_5NBr_2$. Calculated %: Br 31.16.

Condensation of Cotarnine with Malonic Acid and Ammonia

10 g of cotamine and 40 ml of a 12% alcoholic solution of ammonia in a flask equipped with upright condenser was left in a cooling mixture for a half-hour, and 4.5 g of malonic acid then poured in, and the temperature of the bath raised in such a manner that the alcohol distilled off over 3-3.5 hours. The mass remaining in the flask was dissolved in 15 ml of water by heating on a water bath and filtered. Upon cooling, a crystalline precipitate of the unsaturated 2-β-(N-methyl)-aminoethyl-4,5-methylendihydroxy-6-methoxycinnamic unsaturated amino acid (VII) resulted in the amount of 7.2 g (61%). After two recrystallizations from alcohol, and drying in a drying cabinet at

125°, the m.p. was 204-206°. It crystallized with 2 molecules of water. Melting point of the aqueous acid was 121-122°.

Found %: N 4.83, 4.65. $C_{14}H_{18}O_5N$. Calculated %: N 5.00.

The filtrate, after evaporation on a water bath, resinified, but the amino acid was not obtained in the pure state.

Condensation of Cotarnone with Malonic Acid and Ammonia

28 g of cotarnone, 9 ml of 11% alcoholic ammonia solution and 1.6 g of malonic acid were heated on a water bath in a flask equipped with vertical condenser, for 3.5-4 hours. The bath temperature was gradually raised in order that the alcohol and ammonia excess might distill off gradually, and only during the last hour was the bath heated to boiling. The resulting dry residue was repeatedly treated with benzene preheated to 30° and the benzene solution evaporated to 10-12 ml volume; thereupon, the crystals of unsaturated acid (X) separated. The acid dissolved in alcohol, benzene, acetic acid and ether, and decolorized bromine water and potassium permanganate solution. It crystallized out from alcohol or benzene with a m.p. of 177-179°. The analytical data and the gram equivalent value indicated that the substance was 2-vinyl-4,5-methylendihydroxy-6-methoxycinnamic acid. The yield was 1 g (29.7%).

Found %: C 62.81, 62.73; H 5.00, 5.05; g-equiv. 244.1. $C_{13}H_{12}O_5$. Calculated %: C 62.90; H 4.84; g-equiv. 248.

The residue, after isolation of the unsaturated acid (X) was dissolved in 40-50 ml of 5% soda solution, filtered to remove a small resinous precipitate, and was acidified with 10% hydrochloric acid solution to a strongly acid reaction. Thereupon, the dibasic acid separated, apparently being the γ-(2-aldehydo-3-methoxy-4,5-methylendihydroxy)-phenylpropandicarboxylic acid (XI). M.p. was 98° (with decomposition). The yield was 2.2 g (52%).

Found: g-equiv. 162.9. M 325.8. $C_{14}H_{14}O_8$. Calculated: M 310.

The total yield of unsaturated acids was 52.6 + 29.7 = 82.3%. After isolation of the dicarboxylic acid, the solution was evaporated in vacuo. The residue, upon evaporation, resinified, and the β-amino acid was not found.

Bromination of 2-Vinyl-4,5-methylendihydroxy-6-methoxycinnamic Acid

0.7 g of unsaturated acid (X) and 10 ml of dry carbon tetrachloride were placed in a flask equipped with reflux condenser and dropping funnel. The flask was cooled with a mixture of water and ice, and 3 ml of 10% bromine solution in carbon tetrachloride was then gradually added. All of the acid gradually went into solution. During the reaction no gas evolution was observed. The mixture was left overnight at room temperature.

A precipitate, consisting of the tetrabromoderivative of the acid taken, was formed. White crystals with m.p. 150° (from alcohol). The substance was poorly soluble in alkali. Yield was 1.6 g (99.9%).

Found %: C 27.33, 27.49; H 2.24, 2.15. $C_{13}H_{12}O_5Br_4$. Calculated %: C 27.46; H 2.11.

SUMMARY

It has been established that condensation, under the usual Rodionov synthesis conditions, of cotarnine and its derivative, benzoylcotarnine, and of cotarnone, as well as of benzoylhydrastinine, with malonic acid and ammonia, proceeds mainly in the direction of unsaturated acid formation: yield of amino acids is relatively poor.

New compounds which have been synthesized are:

1) the unsaturated 2-β-(N-methyl-N-benzoyl)-aminoethyl-4,5-methylendihydroxy-6-methoxycinnamic acid (III), its mono- and dibromo- derivatives and the ethyl ester;

2) the amino acid, 2-β-(N-methyl-N-benzoyl)-aminoethyl-4,5-methylendihydroxy-β-phenyl-β-alanine, (IV), its hydrochloride, benzoyl and p-nitrobenzoyl derivatives;

3) the unsaturated 2-β-(N-methyl-N-benzoyl)-aminoethyl-4,5-methylendihydroxycinnamic acid (V) and its bromo derivative;

4) 2-β-(N-methyl-N-benzoyl)-aminoethyl-4,5-methylendihydroxy-β-phenyl-β-alanine hydrochloride (VI);

5) 2-vinyl-4,5-methylendihydroxy-6-methoxycinnamic acid (X), the unsaturated acid (VII), and the tetrabromo derivative.

All of the ennumerated compounds have been synthesized and described for the first time.

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* See Consultants Bureau Translation, page 353.

RESEARCH IN THE CHEMISTRY OF CHLOROMYCETIN (LEVOMYCETIN)

II. A STUDY OF SYNTHETIC METHODS AND OF THE SYNTHESIS OF OPTICALLY-ACTIVE ANALOGS OF CHLOROMYCETIN (LAEVOMYCETIN) [1]

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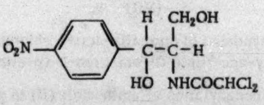
During the past few years, D-threo-1-(p-nitrophenyl)-2-dichloroacetylamino-1,3-propandiol (I) (chloromycetin, chloroamphenicol, laevomycetin) has attracted considerable interest, and has been investigated in detail, both in the medico-biological sense [2] and in the chemical sense [3].



(I)

One of the most intense lines of development of such investigations is a study of the relationship between structure and antibacterial activity in the chloromycetin series. At present methods of synthesis, and the synthesis of a considerable number (several hundred) of analogs and derivatives of this compound have been realized, many of which compounds have been tested biologically [3]. However, this type of research suffers one serious handicap of major proportion The crux of the matter lies in the fact that of the four stereoisomers of 1-(p-nitrophenyl)-2-dichloroacetylamino-1,3-propandiol, only one, namely, the D-threo-isomer (chloromycetin) possesses antibacterial activity. Therefore, a study of the relationship between structure and antibacterial activity for this series of compounds can give comparable results only in the event that the analogs tested possess the same steric configuration as chloromycetin. However, a study of this problem reveals that in a majority of cases compounds have been biologically tested whose steric structure remains obscure, resulting data on which, therefore, cannot be considered to be sufficiently convincing. Furthermore, there are no descriptions for general methods of synthesizing a series of the more important chloromycetin analog types with strictly-defined steric configuration. The only exception is that of the N- and O-acylchloromycetin analogs which can be obtained by acylation of D-threo-1-(p-nitrophenyl)-2-amino-1,3-propandiol, or its steroisomers under conditions which exclude the possibility of inversion or racemization. In the remaining cases, however, the steric structures of synthesized analogs has usually been judged only upon circumstantial evidence. To illustrate, if a given synthetic procedure* leads mainly to formation of D,L-threo-1-(p-nitrophenyl-)-2-dichloroacetylamino-1,3-propandiol (chloromycetin racemate), and not to its diastereoisomer, it has then been considered that all analogs likewise synthesized by this procedure would also possess the threo configuration. Such conclusions are of course not entirely convincing, particularly in view of the fact that even a small change in synthetic conditions can lead not to formation of the chloromycetin racemate, but instead to its biologically-inactive diastereoisomer** (for details see [3]).

Relative to that which has been stated above, the authors have attempted to develop general synthetic procedures for certain types of chloromycetin analogs which possess strictly-defined steric configuration, in order to obtain correlative data for solution of the problem of relation between structure and antibacterial activity for the series of compounds in question. At the same time we carried out another objective — to elucidate the steric structures of certain chloromycetin analogs obtained earlier by methods already described in the literature.

There are described below two synthetic methods developed by the authors for obtaining optically-active analogs of D-threo-1-(p-nitrophenyl)-2-dichloroacetylamino-1,3-propandiol (chloromycetin), differing from this compound by the presence of other substituents in the p-position of the benzene ring, in place of the nitro group.

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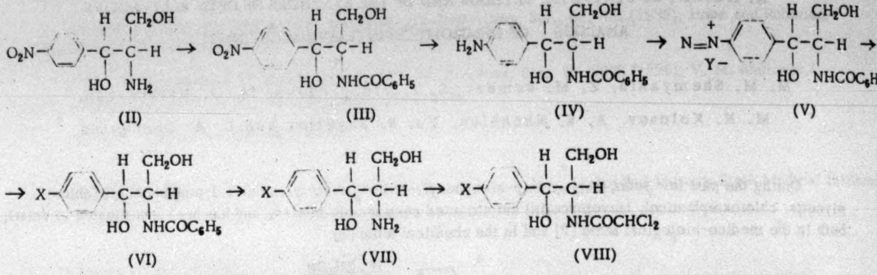
* For example, the Long and Troutman synthesis which has found extensive application, starts with p-substituted acetophenones [4].

** When for example synthesis is carried out, starting with p-nitrobenzaldehyde and glycine ester [5].

The two methods make it possible to proceed further with a compound of known steric configuration, and which does not change during the procedure of synthesizing the indicated analogs.

The first method is presented in Scheme 1.

Scheme 1



According to this chart, the synthesis of optically-active chloromycetin analogs of the general type (VIII) is realized by starting with the readily-accessible D- or L-threo-1-(p-nitrophenyl)-2-amino-1,3-propandiol (II).*

The first stage of synthesis —benzoylation of aminodiols (II) to give the corresponding N-benzoyl derivatives (III)— should be carried out by using the earlier-described procedure [6]. Yields reach 70-75%.

The second stage of synthesis —conversion of N-benzoyl nitro derivatives (III) to the amino compounds (IV)— can be effected by hydrogenation at 70-80° and 50 atmospheres in the presence of a nickel catalyst base; yield was 90-95% of theory. The reduction process can be carried out at room temperature and normal pressure, but in such case reaction proceeds a great deal slower.

The third stage of synthesis —diazotization of the amino compounds (IV)— is carried out in mineral acid solutions at 0-5°; however, this process proceeds very slowly (3-4 hours). The conditions of diazotization have to be modified somewhat, depending upon the type of radical which is to replace the diazo group. It should be mentioned that diazonium salts of the type (V), are quite stable in aqueous solutions, especially at low temperatures.

The fourth stage of synthesis —replacement of the diazo group in diazonium salts of the type (V) by various atoms or radicals (H, Cl, I, OH, CN, NO_2, AsO_3H_2)— can, in a number of cases, be carried out according to standard procedures, but at times (with replacement by I, OH, CN) it is necessary to maintain specific conditions.** Compounds of the general type (VI) which result from this reaction are often obtained satisfactorily (from 50 to 80% in the case of diazo group replacement by H, Cl, I and CN); however, with OH replacement the yield drops to 40%, and upon replacement with AsO_3H_2, to 20%. Diazo compounds of the type (V) readily undergo azo coupling, for example with β-naphthol, the corresponding azo dye resulting in 85% yield.

The fifth stage of synthesis —rupture of the N-benzoyl group in compounds of the general type (VI)— can, in a number of cases, be carried out by heating for several hours with 20% HCl. From chloro- and iodo-substituted compounds (VI), where X = Cl or I, there are formed the corresponding aminodiols, of general type (VII) in about 55% yield. With nitriles (VI: X = CN), rupture of the benzoyl group is accompanied by hydrolysis of the nitrile group to the carboxyl group, which results in compounds found to be the internal salt (yield 65%).

$$\bar{O}OC \cdot C_6H_4CHOHCH(\overset{+}{N}H_3)CH_2OH.$$

However, in the case of hydroxy compounds (VI: X = OH), 15 minutes heating with 1% HCl suffices to rupture the benzoyl group; even under these conditions, however, hydrolysis is accompanied by such molecular changes that isolation of the individual compounds is difficult.

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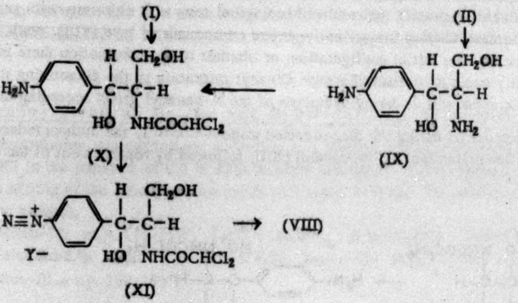
* For the sake of brevity, there are given in Schemes 1 and 2 formulas for the D-threo- series of compounds only.

** Thus, the replacement of diazo group by iodine proceeds satisfactorily only in the presence of KI in highly diluted solution, wherein the reaction should first be carried out at 0° and then at 20°. In synthesizing hydroxy compounds, it is necessary that initial pH value for the diazo solution be in the range 5-6, and the process itself carried out at 70-90°. On the other hand, replacement of the diazo group by the nitrile group proceeds satisfactorily in the presence of cuprous cyanide only when the initial pH for the medium is about 7 and the temperature about −5°.

The last (sixth) stage of synthesis – N-dichloroacetylation of aminodiols of the type (VII) to produce the optically-active chloromycetin analogs, of general type (VIII)– was achieved by two procedures, depending upon the character of the substituent situated in the para-position of the benzene ring. In the case of chloro- and of iodo-substituted aminodiols (VII: X = Cl or I), this reaction was carried out by heating them for a short period of time with the methyl ester of dichloroacetic acid at 90-95° (yield from 50-70%). However, in the case of carboxy-substituted aminodiols (VII: X = COOH) which are not capable of reacting with $Cl_2CHCOOCH_3$, even at 130°, the dichloroacetylation was then carried out by means of an ether solution of the dichloroacetic acid chloroanhydride in the presence of an aqueous solution of K_2CO_3 (yield about 70%).

Since the synthesis of chloromycetin analogs according to Scheme I is carried out via a large number of intermediate stages, and since some compounds of the type (VIII) (for example containing the cyano group) cannot be synthesized at all by this method, the authors developed a second procedure for synthesis of chloromycetin analogs of the type (VIII), as presented in Scheme 2.

Scheme 2



The great advantage of this chart of synthesis, as compared with the preceding, is the absence of hydrolytic stages and of dichloroacetylation, for here, in contrast to Scheme 1, the diazotization reaction and replacement of the diazo group by various atoms and radicals is carried out on N-dichloroacetyl derivatives of (X) type, which is found to be a quite accessible compound, which is not so for the N-benzoyl derivatives of type (IV).

At first, N-dichloroacetylation of the type compound (X) was carried out, proceeding from D- and L-threo-1-(p-nitrophenyl)-2-amino-1,3-propandiols (II) which were catalytically reduced to the corresponding diamines of the type (IX), with 90% yield, under conditions of (III) and (IV) hydrogenation. However, selective dichloroacetylation of diamines (IX) could be carried out only with the aliphatic amino groups, reacting them with the methyl ester of dichloroacetic acid at room temperature for 24 hours, with subsequent isolation of D- and L-threo-1-(p-aminophenyl)-2-dichloroacetyl-amino-1,3-propandiols (X) in their hydrochloride form (yields up to 25%). It was found later, however, to be more convenient to synthesize a compound of type (X) by reduction of D- and L-threo-1-(p-nitrophenyl)-2-dichloroacetylamino-1,3-propandiols (I) in the presence of a nickel catalyst base, at normal pressure and room temperature. It was established that if hydrogenation is terminated after absorption of one-half the theoretical hydrogen volume, then rupture of chlorine from the dichloroacetyl group occurred only to the extent of 2-3%, and the D- and L-threo-1-(p-aminophenyl)-2-dichloroacetylamino-1,3-propandiols (X) which form can then be readily isolated in the form of pure hydrochlorides (yields 35-40%) and at the same time about 25% of the initial nitro compound (I) being recovered.

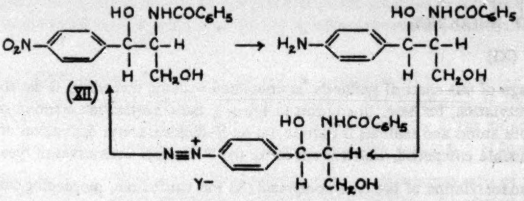
Diazotization of N-dichloroacetyl derivatives (X) is accomplished under the same conditions as with the N-benzoyl- compound (IV), but proceeds more rapidly. The diazonium salts of (IX) which result are more difficult to dissolve in water than salts of the original amines, and upon diazotizing concentrated solutions, they precipitate out. In the dry state these salts are very stable; thus, for example, the chlorides were stored in the dry state at room temperature for several weeks without noticeable decomposition. However, in aqueous solutions, diazonium salts of the type (XI) are more reactive than their benzoyl analogs (V), and it is, therefore, more expedient to carry out replacement of the diazo group in them at lower temperatures. It is true that yields of the chloromycetin analogs (VIII) formed are somewhat lower than the N-benzoyl derivatives (VI); thus, replacement of a diazo group by Cl, OH, and CN proceeds with a yield of 45-50%, and for AsO_3H_2 in only 16% yield. It is very intimately bound up with the fact that N-benzoyl derivatives (VI) crystallize better, and are more easily purified, than the N-dichloroacetyl derivatives (VIII).

To study the relation between structure and antibacterial activity for the chloromycetin series, it was of interest to obtain such compounds of the type (VIII) as those in which the nitro group is separated from the benzene ring of the chloromycetin molecule by a conjugated multiple bond system. Such compounds were synthesized by the authors from D- and L-threo-1-(p-aminophenyl)2-dichloroacetylamino-1,3-propandiols (X) by their condensation with p-nitrobenzaldehyde and p-nitronitrosobenzene, Schiff's bases (VIII; $X = 4\text{-}O_2NC_6H_4CH = N-$) resulting in 62% yield, and nitroazo compounds (VIII; $X = 4\text{-}O_2NC_6H_4N = N-$) in 56% yield. Furthermore, nitrohydroxyazo compounds (VIII; $X = 3,4\text{-}(O_2N)(HO)C_6H_3N = N-$), obtained from D- and L-threo-amines (X), were synthesized by diazotization and subsequent coupling with o-nitrophenol (yield 29%).

It should be pointed out that despite relatively low yields, synthesis of chloromycetin analogs of the type (VIII), carried out according to Scheme 2, is very convenient because of the simplicity and brevity, since their synthesis is reduced to two stages: 1) the synthesis of amino compounds (X), and 2) their conversion via diazo compounds or by condensation, to chloromycetin analogs of the type (VIII).

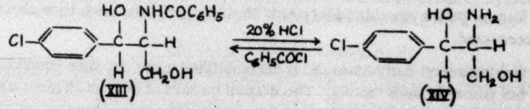
As was indicated above, it is imperative to have complete, accurate data concerning steric structures of the substances investigated in order to evaluate accurately the results of biological tests with chloromycetin analogs. It was necessary, in this regard, to determine whether the optically-active compounds of type (VIII), synthesized in accordance with Schemes 1 and 2, maintained the initial configuration, or whether in their formation there took place Walden inversion. The latter could only occur as a result of N ⟶ O^1-acyl migration in the diazotizing stages, which can be accomplished in both schemes, as well as during hydrolysis of the N-benzoyl group according to Scheme 1*.

In order to prove that no inversion occurs during the diazotization stage of Scheme 1, the authors reduced and diazotized L-threo-1-(p-nitrophenyl)2-benzoylamino-1,3-propandiol (XII), followed by replacement of the diazo group by the nitro group:



The original L-threo-nitro compound (XII) resulted, from which it follows that diazotization of threo-1-(p-aminophenyl)-2-benzoylamino-1,3-propandiols is not accompanied by inversion of their molecular configuration.

No inversion upon acid hydrolysis of the N-benzoyl derivatives of type (VI) was demonstrated by the authors for L-threo-1-(p-chlorophenyl)-2-benzoylamino-1,3-propandiol (XIII). Upon heating this compound with 20% HCl, the corresponding aminodiol (XIV) resulted, benzoylation of which lead to formation of the original L-threo- compound (XIII):



Hence, synthesis of chloromycetin analogs of the type (VII) as carried out by Scheme 1, was not accompanied by Walden inversion, and lead to compounds of the same configuration as existed for the original D- and

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* It is known that under the influence of acid reagents, the N-acyl derivative of α-amino alcohols rearranges to salts of the corresponding O-acyl derivatives, and that this rearrangement may be accompanied by inversion in the configuration of that asymmetric carbon atom which is attached to the hydroxyl group. In a series of p-substituted threo-1-phenyl-2-acylamino-1,3-propandiols having the cis-configuration, the N ⟶ O^1-acyl migration usually takes place with preservation of the configuration [7], but isolated cases are known where in the course of this reaction inversion occurs [8].

L-threo-1-(p-nitrophenyl)-2-amino-1,3-propandiols (II).

Synthesis of type (VIII) compounds was carried out according to Scheme 2, which also took place with preservation of steric configuration for the molecules. This was demonstrated by the authors through conversion of L-threo-1-(p-aminophenyl)2-dichloroacetylamino-1,3-propandiol (X) into the p-chlorosubstituted analog of chloromycetin (VIII: X = Cl) belonging to the L-threo- series, and which was synthesized earlier according to Scheme 1 from L-threo-nitroaminodiol (II).

Inasmuch as synthesis of chloromycetin analogs according to Schemes 1 and 2 leads to formation of sbustances of strictly-defined configuration, it can be used as a method for proof of the steric structures for various compounds of the type (VIII) resulting from other procedures described in the literature. Thus, for example, the authors obtained corresponding racemates by combining the D- and L-isomers of p-chloro and p-iodo-substituted chloromycetin analogs (VIII: X = Cl or I) which were synthesized according to Schemes 1 and 2, and these racemates were found to be identical with racemic p-chloro and p-iodo-substituted chloromycetin analogs which were synthesized by proceeding from p-chloro- and p-iodo-acetophenones according to the method of Long and Troutman [9] published earlier. By the same fact was proved definitely for the first time that the Long and Troutman method applied to these compounds leads to chloromycetin analogs belonging to the threo- series.

EXPERIMENTAL

1. Benzoylation of D-, L- and D,L-threo-1-(p-Nitrophenyl)-2-amino-1,3-propandiols (II)

Benzoylation was carried out according to a method published earlier [5] for reacting aminodiols (II) with C_6H_5COCl in the presence of 0,5 N KOH solution and ether. If this reaction is carried out with continuous and very rigorous stirring of the mixture, then yields will reach 70-75%. The resulting substances were purified by crystallization from alcohol.

D-threo-III: m.p. 171-172°; $[\alpha]_D^{18}$ −120.5° (c 1.3 in CH_3OH). Found %: C 60.53; H 5.14; N 8.94. $C_{16}H_{15}O_5N_2$. Calculated %: C 60.75; H 5.10; N 8.86. L-threo-III: m.p. 171-172°; $[\alpha]_D^{17}$ + 121.5° (c 2.1 in CH_3OH). D,L-threo-III, m.p. 162-163°.

2. Reduction of D-, L- and D,L-threo-1-(p-nitrophenyl)-2-benzoylamino-1,3-propandiols (III).

40 g of D-, L-, or D,L-threo-III in 300 ml of alcohol was hydrogenated in the presence of 5 g of nickel catalyst base. Reaction was carried out in a revolving autoclave (1 liter in volume) at 75-80° and an initial pressure of 40-50 atmospheres. After the cessation of H_2 absorption, the solution while hot was removed from catalyst by filtration and cooled. The resulting crystals were filtered off and washed with alcohol. The weight was 26.5-27.5 g. Another 6.5-7.0 g of substance was isolated from the mother liquor after evaporation. Total yield was 33-34.5 g (91-95%). The resulting amino compound was recrystallized from alcohol.

D-threo-IV: m.p. 170-171°; $[\alpha]_D^{18}$ −100.5° (c 1.1 in CH_3OH). L-threo-IV: m.p. 170-171°; $[\alpha]_D^{17}$ + 99.5° (c 1.9 in CH_3OH). Found %: C 67.36; H 6.32; N 10.03. $C_{16}H_{18}O_3N_2$. Calculated %: C 67.14; H 6.34 N 9.79. D,L-threo-IV: m.p. 151-152°.

3. Diazotization of D- and of L-threo-1-(p-Aminophenyl)-2-benzoylamino-1,3-propandiols (IV), and Replacement of the Diazo Group in the Diazonium Salts (V)

a) L-threo-VI (X = H) Synthesis. 6 g of L-threo-IV was dissolved in 60 ml of 5% H_2SO_4 and diazotized at 0-5° with 20% $NaNO_2$ solution. The excess HNO_2 was decomposed with urea. 60 ml of alcohol and 6 ml of concentrated H_2SO_4 were added to the diazo solution, and 0.75 g of a copper-bronze added at 0-5°. After cessation of N_2 evolution the reaction mass was heated at 50-60° to complete decomposition of the diazonium salt (20-30 minutes), filtered and neutralized with 20% NaOH solution to a pH of 5.5-6.0. The reaction product was extracted with ethyl acetate, the alcohol having been distilled off in vacuo. The extract was washed with 5% NaOH solution and water, dried with Na_2SO_4, treated with carbon, with heat and evaporated to 10-12 ml volume. The precipitate which resulted upon cooling was filtered off and washed with ethyl acetate, and then with ether. Yield was 3.1 g (55%); m.p. 180-183°. The substance was purified by recrystallization from a mixture of alcohol and ethyl acetate (1:2).

L-threo-VI (X = H): m.p. 184-186°; $[\alpha]_D^{20}$ + 98.9° (c 2.0 in CH_3OH). Found %: C 70.62; H 6.50; N 5.18. $C_{15}H_{17}O_3N$. Calculated %: C 70.83; H 6.32; N 5.16.

L-threo-VI (X = H) was synthesized from L-threo-IV via L-threo-V and by reduction of the latter with H_3PO_2; in this case, however, a more complex purification of the substance was necessary, which resulted in considerably lowered yield.

The L-threo-VI (X = H) O,O-diacetyl derivative was obtained by heating the corresponding diol with acetic anhydride and pyridine. After recrystallization from 50% alcohol, m.p. was 146-148°.

Found %: N 3.90. $C_{20}H_{21}O_5N$. Calculated %: N 3.94.

b) D- and L-threo-VI (X = Cl) Synthesis. 5 g of D- or L-threo-IV was suspended in 50 ml of 17% HCl, and was diazotized at 0-5° with 1.75 g of $NaNO_2$ solution in 7 ml of water. The excess HNO_2 was decomposed with urea. The diazo solution was added, with stirring, to Cu_2Cl_2 (prepared from 6 g of $CuSO_4 \cdot 5H_2O$ [10]) in 10 ml of 28% HCl solution precooled to 0°, and the reaction mass left at room temperature overnight. The precipitate formed was stirred and washed with water, dried and heated with 150 ml of ethyl acetate. The solution was filtered off, heated with carbon and evaporated to small volume. An almost pure chloro derivative crystallized out upon cooling. Yield was 4.0 g (75%); m.p. 170-171°. The substance was recrystallized from 50% alcohol.

D-threo-VI (X = Cl): m.p. 171-172°; $[\alpha]_D^{16}$ −102.8° (c 1.5 in CH_3OH). L-threo-VI (X = Cl): m.p. 171-172°; $[\alpha]_D^{19}$ + 102.4° (c 4.5 in CH_3OH). Found %: C 62.96; H 5.51; N 4.63. $C_{16}H_{15}O_3NCl$. Calculated %: C 62.83; H 5.24; N 4.58.

In some cases, under the conditions described above, D- and L-threo-VI (X = Cl) were formed with m.p. 156° (instead of m.p. 171-172°). They had the same specific rotation value, and upon hydrolysis gave the same aminodiols as for compounds with m.p. 171-172°.

c) D-, L-, and D,L-threo-VI (X = I) Synthesis. 5 g of D-, L-, and D,L-threo-IV was dissolved in 165 ml of 1.5% H_2SO_4, 200 g of ice added, and diazotized at 0° with the theoretical quantity of 20% $NaNO_2$ solution. 4 g of KI in 50 ml of water was added, with cooling to 0°, and stirring, to the resulting diazo solution, and the reaction mixture left at 0° for 16 hours. The resins which separated were extracted with ethyl acetate (2 times in 75 ml portions) and the aqueous solution left at 20° to complete decomposition of the diazo compound, for which about 48 hours was required. The resulting precipitate was filtered off, washed with ethyl acetate, and dried; the weight was 4.0 g. The aqueous solution was extracted with ethyl acetate (3 times in 100 ml portions), and the extract washed with 5% $Na_2S_2O_3$ solution and water, followed by drying with Na_2SO_4 in the presence of carbon. The solution was evaporated in vacuo, the residue stirred with 10 ml of ethyl acetate and the precipitate filtered off; weight was 0.65 g. After recrystallization of the total resulting substance from 100 ml of 30% alcohol, there resulted 3.5 g (50%) of iodo derivative.

D-threo-VI (X = I): m.p. 178-179°; $[\alpha]_D^{22}$ −87.3° (c 0.5 in CH_3OH). L-threo-VI (X = I): m.p. 178-179°; $[\alpha]_D^{19}$ + 86.2° (c 1.1 in CH_3OH). Found %: C 48.55; H 4.26; N 3.41. $C_{16}H_{16}O_3NI$. Calculated %: C 48.37; H 4.06; N 3.53. D,L-threo-VI (X = I): m.p. 173.5-174.5°. (The same substance was obtained from D- and L-threo-VI (X = I) by dissolving in and subsequently recrystallizing from 30% alcohol.

d) L-threo-VI (X = OH) Synthesis. 10 g of L-threo-IV was dissolved in 100 ml of 10% H_2SO_4 and diazotized at 0-5° with 2.5 g of $NaNO_2$ solution in 10 ml of water. The excess HNO_2 was decomposed with urea. The diazo solution was neutralized with $NaHCO_3$ to a pH of 5.5-6.0, heated at 70-90° to complete decomposition of the diazonium salt, decolorized with carbon, and cooled. 5 g of substance resulted (m.p. 183-185° with decomposition), which was recrystallized from 25% alcohol. Yield was 4 g (40%).

L-threo-VI (X = OH): m.p. 196-198° with decomposition; $[\alpha]_D^{19}$ + 103° (c 2.1 in CH_3OH). Found %: C 67.06; H 6.00; N 5.10. $C_{16}H_{17}O_4N$. Calculated %: C 66.88; H 5.99; N 4.88.

e) D- and L-threo-VI (X = CN) Synthesis. 25 g of D- or L-threo-IV was dissolved in 250 ml of 5% H_2SO_4 and diazotized at 0-5° with 6.25 g of $NaNO_2$ solution in 25 ml of water. The diazo solution was neutralized with $NaHCO_3$ to a pH of 6.0-6.5, and gradually added with stirring to a cuprous cyanide solution* which was under a layer of toluene (250 ml) and precooled to −5°. After completion of the diazonium salt decomposition, the reaction mass was stirred for another 15 minutes and separated from the resinous substance which came out by filtration. The toluene layer was separated and the aqueous solution extracted with ethyl acetate (4 times in 75 ml portions). The extract was dried with Na_2SO_4, evaporated to 40-50 ml volume and diluted with 5 times the volume of benzene; 4.7 g of nitrile precipitated, with m.p. 136-137.5°. The resinous substance filtered off from the reaction mass was dissolved in ethyl acetate, the solution clarified with carbon, and the solvent distilled off. The residue, when stirred with benzene, crystallized. It was heated with water (3 times in 500 ml portions) and the hot, aqueous solution filtered off and left overnight; the oily substance which separated was purified by repeating the described treatment with boiling water. The combined water solution was decolorized by heating with carbon and then extracted with ethyl acetate

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* The latter was obtained by mixing 55 g of KCN solution in 110 ml of water with a suspension of Cu_2Cl_2 (from 63 g of $CuSO_4 \cdot 5H_2O$ [10]) in 100 ml of water, and by neutralizing the solution formed with 10% CH_3COOH to a pH of 7.0-7.5.

(3 times in 150 ml portions). The extract was evaporated to 75-100 ml volume and diluted with 5 times the volume of benzene. 16.4 g of almost pure nitrile resulted, with m.p. 136-137.5°. The total yield was 21.1 g (82%). The substance was recrystallized from water.

D-threo-VI (X = CN): m.p. 139-140°; $[\alpha]_D^{20}$ −130.4° (c 5.2 in CH_3OH). L-threo-VI (X = CN): m.p. 139-140°; $[\alpha]_D^{20}$ + 129.8° (c 5.2 in CH_3OH). Found %: C 69.05; H 5.74; N 9.57. $C_{17}H_{16}O_3N_2$. Calculated %: C 68.92; H 5.46; N 9.46.

f) L-threo-VI (X = NO_2) Synthesis. 2.8 g of L-threo-IV was dissolved in 14 ml of 10% H_2SO_4 and diazotized at 0-5° with 20% $NaNO_2$ solution. The diazo solution was neutralized with $CaCO_3$ to disappearance of an acid reaction to Congo red, and filtered. 1.5 g of $Na_3Co(NO_2)_6$ was dissolved in the filtrate at room temperature and the solution cooled to 3-5°. After 15 minutes the liquid was decanted off from the precipitate which formed, and a suspension of 0.4 g Cu_2O in a solution of 1 g of $NaNO_2$ and 1 g of $CuSO_4 \cdot 5H_2O$ in 6 ml of water added with cooling and stirring. After cessation of N_2 evolution, stirring was stopped and the reaction mass left for 10-12 hours. The nitro compound extracted with ethyl acetate (7-8 times with 30 ml portions), the extract washed with 3% H_2SO_4, 5% $NaHCO_3$ solution, water, and then dried with Na_2SO_4, clarified with charcoal, and concentrated. The residue was heated with 15 ml of water, the aqueous solution treated with carbon while heating, and then cooled. The resulting precipitate was purified by recrystallization from water with charcoal, and then with 20% alcohol. The resulting nitro compound had a m.p. of 169-170° and $[\alpha]_D^{20}$ + 122° (c 1.3 in CH_3OH); it was identical with L-threo-III described in Experiment 1.

g) L-threo-VI (X = AsO_3H_2) Synthesis. 5 g of L-threo-IV was dissolved in 165 ml of 1.5% H_2SO_4 and diazotized at 0-5° with 1.25 g of $NaNO_2$ solution in 5 ml of water. The excess of NHO_2 was decomposed with urea. The diazo solution was neutralized with $NaHCO_3$ to a pH of 6.5, and 0.1 g of $CuSO_4 \cdot 5H_2O$, 2.2 g As_2O_3 and 4.4 g of Na_2CO_3 in 16 ml of water added dropwise over a period of 3 hours to the solution, with stirring, at 15°. The reaction mixture was stirred for another hour or more, filtered, neutralized with concentrated HCl to a pH of 7, evaporated in vacuo, and then filtered again. The filtrate (5-7 ml) was gradually acidified with concentrated HCl to an acid reaction with Congo red, whereby resins separated at first, which were filtered off, after which the precipitate of arsonic acid (1.88 g) separated. After recrystallization from 30% alcohol, the yield was 1.53 g (22%).

L-threo-VI (X = AsO_3H_2) decomp. 142-143°; $[\alpha]_D^{22}$ + 88.5° (c 2.1 in CH_3OH). Found %: As 18.45; N 3.28. $C_{16}H_{18}O_6NAs$. Calculated %: As 18.95; N 3.54.

h) L-threo-VI (X = 1-[2-(HO)$C_{10}H_6$]N = N−) Synthesis. 2 g of L-threo-IV was dissolved in 20 ml of 5% H_2SO_4 and diazotized at 0-5° with 0.5 g of $NaNO_2$ solution in 1.5 ml of water. The excess HNO_2 was decomposed with urea. The diazo solution was added, with stirring, to 1.3 g of β-naphthol solution precooled to 0°, plus 0.36 g of NaOH and 1.5 g of Na_2CO_3 in 40 ml of water. The resulting red precipitate was filtered off and washed with water, followed by methanol. The yield was 2.6 g (84 %). The substance was purified by recrystallization from a large volume of methanol.

L-threo-VI (X = 1-[2-(HO)$C_{10}H_6$]N = N−): decomposition point 224-226°; $[\alpha]_D^{18}$ + 180° (c 0.3 in dioxane). Found %: C 70.39, H 5.43; N 9.83. $C_{26}H_{23}O_4N_3$. Calculated %: C 70.75; H 5.21; N 9.52.

4. Hydrolysis of p-Substituted D- and L-threo-1-Phenyl-2-benzoylamino-1,3-propandiols (VI)

a) D- and L-threo-VI (X = Cl) Hydrolysis. 2.5 g of D- or L-threo-VI (X = Cl) was heated for 4 hours with 25 ml of 20% HCl. Benzoic acid was extracted with ether, the aqueous solution heated with carbon and evaporated in vacuo to dryness. The residue was dissolved in 3 ml of water and concentrated NH_3 solution added. The base which separated was recrystallized with charcoal from 15 ml of water. 0.92 g (56%) of pure aminodiol resulted.

D-threo-VII (X = Cl): m.p. 145-147°; $[\alpha]_D^{20}$ −33.6° (c 2.5 in 5% HCl). L-threo-VII (X = Cl): m.p. 145-147°; $[\alpha]_D^{20}$ + 35.0° (c 4.0 in 5% HCl). Found %: C 53.75; H 6.22; N 6.86. $C_9H_{12}O_2NCl$. Calculated %: C 53.60; H 6.01; N 6.95. D,L-threo-VII (X = Cl): m.p. 122-123°, (this compound was prepared from D- and L-threo-VII (X = Cl) by combining and then recrystallizing from water).

0.2 g of L-threo-VII (X = Cl) was benzoylated under the conditions of Experiment 1. 0.2 g (66%) of L-threo-VII (X = Cl) resulted, identical with the substance which was described in Experiment 3b.

b) D-, L- and D,L-threo-VI (X = I) Hydrolysis. 3.5 g of D-, L- or D,L-threo-VI (X = I) was heated for 10 hours with 35 ml of 10% HCl. The solution was clarified by heating with carbon and after extraction of benzoic acid with ether, concentrated NH_3 solution was added. The oily substance which separated was extracted with ethyl acetate, the extract heated with carbon, dried with Na_2SO_4, and evaporated in vacuo. The residue was mixed with a small volume of ethyl acetate, the resulting precipitate filtered off, and washed with the same solvent. Yield was 1.42 g (55%). The D- and L-isomers were recrystallized from 15% alcohol, and the D,L-compound recrystallized from water.

D-threo-VI (X = I): m.p. 103-104°. L-threo-VI (X = I): m.p. 103-104°; $[\alpha]_D^{20}$ + 23.6° (*c* 1.9 in 5% HCl). Found %: C 36.56; H 4.14; N 4.14; N 4.31. $C_9H_{12}O_2NI$. Calculated %: C 36.87; H 4.09; N 3.78. D,L-threo-VII (X = I): m.p. 180-181°.

c) D- and L-threo-VI (X = CN) Hydrolysis. 15 g of D- or L-threo-VI (X = CN) was boiled for 8 hours with 225 ml of 20% HCl. The benzoic acid was extracted with ether, the aqueous solution heated with carbon, and the solution evaporated in vacuo to dryness. The residue was dissolved in 20 ml of water, the solution neutralized with concentrated NH_3 solution to pH 5-6, and the resulting precipitate filtered off. The weight was 4.6 g. An equal volume of concentrated HCl was added to the filtrate, the solution boiled for 8 hours, and treated as described above. Another 2,4 g was obtained. The total yield was 7,0 g (65%). The substance was recrystallized from 280 ml of water and the solution partially evaporated before cooling.

D-threo-VII (X = COOH): decomposition point was 348-349° – the capillary being placed in the block at 320°; $[\alpha]_D^{22}$ – 32.4° (*c* 4.0 in 5% HCl). L-threo-VII (X = COOH); decomp. 348-349°; $[\alpha]_D^{22}$ + 32.6° (c 4.0 in 5% HCl). Found %: C 56.37; H 6.49; N 6.60. $C_{10}H_{13}O_4N$. Calculated %: C 56.87; H 6.16; N 6.63.

These substances were found to be internal salts. They are insoluble in organic solvents, poorly soluble in water, and readily soluble in aqueous solutions of acid and of alkali; they do not undergo N-dichloroacetylation upon heating with $Cl_2CHCOOCH_3$, but they can be N-acylated by reacting with $Cl_2CHCOCl$ in the presence of an aqueous solution of K_2CO_3.

5. Dichloroacetylation of p-Substituted D- and L-threo-1-Phenyl-2-amino-1,3-propandiols (VII)

a) D- and L-threo-VIII (X = Cl) Synthesis. 2.7 g of D- or L-threo-VII (X = Cl) and 2.9 g of $Cl_2CHCOOCH_3$ were heated to 90° and kept at this temperature for 5 minutes after dissolution of the substance. The viscous mass was stirred with heptane (3 times in 5 ml portions), dissolved in 2-3 ml of dichloroethane, and after adding 3 ml of heptane, was left overnight. Another 3-5 ml of heptane was added to the resulting precipitate, the precipitate filtered off and recrystallized from dichloroethane, and then from water. The yield was 1.95 g (47%).

D-threo-VIII (X = Cl): m.p. was 92-93°; $[\alpha]_D^{23}$ + 8.2° (*c* 7.1 in CH_3OH). L-threo-VIII (X = Cl): m.p. 92-93°; $[\alpha]_D^{17}$ – 9.0° (*c* 3.5 in CH_3OH). Found %: C 42.41; H 4.06; N 4.49. $C_{11}H_{12}O_3NCl_3$. Calculated %: C 42.26; H 3.87; N 4.48. D,L-threo-VIII (X = Cl): m.p. 119-120° (this compound being prepared from D- and L-threo-VIII (X = Cl) by combining them and then recrystallizing from water).

b) D- and L-threo-VIII (X = I) Synthesis. 0.5 g of D- or of L-threo-VII (X = I) and 0.4 g of $Cl_2CHCOOCH_3$ were heated for 15 minutes at 95°, and kept at this temperature for 5 minutes. The reaction mass was cooled and stirred with 5 ml of heptane. The precipitate was filtered off, washed with heptane, and recrystallized from water. The yield was 0.5 g (73%).

D-threo-VIII (X = I): m.p. 103-104°; $[\alpha]_D^{22}$ + 9.7° (*c* 3.5 in CH_3OH). L-threo-VIII (X = I): m.p. 103-104°; $[\alpha]_D^{17}$ – 10.8° (*c* 3.5 in CH_3OH). Found %: C 32.41; H 2.99; N 3.57. $C_{11}H_{12}O_3NCl_2I$. Calculated %: C 32.68; H 2.97; N 3.46. D,L-threo-VIII (X = I): m.p. 122-123° (this compound being prepared from D- and L-threo-VIII (X = I) by combining them and then recrystallizing from water).

c) D- and L-threo-VIII (X = COOH) Synthesis. 60 ml of ether was added to a solution of 4 g of D- or L-threo-VII (X = COOH) and 30 g of K_2CO_3 in 60 ml of water. The mixture was cooled to –5°, and 16 g of $Cl_2CHCOCl$ solution in 30 ml of absolute ether added with stirring for 2 hours. The reaction mass was filtered off, acidified with 20% HCl to a pH of 4-4.5, and extracted repeatedly with ethyl acetate. The unreacted aminodiol which separated during extraction was filtered off, washed with water, and dried. Weight was 2.3 g. The ethyl acetate solution was evaporated to dryness in vacuo. 1.85 g of pure substance resulted; yield was 71% (calculating on the basis of unreacted aminodiol). The substance was crystallized from water.

D-threo-VIII (X = COOH): m.p. 190-191°; $[\alpha]_D^{25}$ + 12.0° (*c* 3.5 in CH_3OH). L-threo-VIII (X = COOH): m.p. 190-191°; $[\alpha]_D^{20}$ – 13.9° (*c* 5.3 in CH_3OH). Found %: C 44.55; H 4.00; N 4.48. $C_{12}H_{13}O_5NCl_2$. Calculated %: C 44.74; H 4.08; N 4.35. D,L-threo-VIII (X = COOH): m.p. 188-189° (this compound being prepared from D- and L-threo-VIII (X = COOH) by combining them and subsequently recrystallizing from water).

6. Synthesis of D- or of L-threo-1-(p-Aminophenyl)-2-dichloroacetylamino-1,3-propandiols (X)

a) D- and L-threo-II Reduction. 50 g of D- or L-threo-II in 350 ml of alcohol was hydrogenated in the presence of 10 g of nickel catalyst base. Reaction was carried out in a revolving autoclave (of 1 liter volume) at 75-80° at an initial pressure of 40-50 atmosphere. While hot, the solution was removed from catalyst by filtration, evaporated in vacuo to the beginning of crystallization, and cooled. The resulting crystals were filtered off and washed with alcohol. Weight was 28-29 g. 10.5-11 g of substance was isolated after evaporation from mother liquor. Total yield was 39-39.5 g (90-92%). The resulting diamino compound was recrystallized from alcohol.

D-threo-IX: m.p. 135-136°; $[\alpha]_D^{22}$ −28.8° (c 9.4 in CH_3OH). L-threo-IX: m.p. 135-136°; $[\alpha]_D^{20}$ + 27.5° (c 10.2 in CH_3OH). Found %: C 59.45; H 7.82; N 15.35. $C_9H_{14}O_2N_2$. Calculated %: C 59.34; H 7.77; N 15.38.

b) D- and L-threo-IX Dichloroacetylation. 15 g of D- or L-threo-IX was dissolved in 150 ml of absolute methanol in 30 ml of $Cl_2CHCOOCH_3$ purified by pyridine. The mixture was left at 18 23° for 24 hours. The solvent and $Cl_2CHCOOCH_3$ excess were distilled off completely in vacuo at 25-30°, and the residue stirred with ethyl acetate (6 times in 50 ml portions). The solution was left for 1-2 hours, filtered off from the resins which formed, washed with water (4 times in 50 ml portions) and dried with Na_2SO_4 overnight at 0-5°, and evaporated in vacuo to a volume of 50-60 ml. The HCl solution in absolute methanol was added, the resulting precipitate filtered off, and washed, first with methanol, and then with ether. For purification, the substance was dissolved in 6 times the volume of absolute methanol and absolute ether added; a crystalline precipitate gradually formed. Yield was 6.7 g (25%). The hydrochloride of the amino compounds (X) gradually decomposed without melting upon heating.

D-threo-X hydrochloride: $[\alpha]_D^{18}$ + 8.1° (c 9.6 in CH_3OH). L-threo-X hydrochloride: $[\alpha]_D^{20}$ −8.5° (c 5.3 in CH_3OH). Found %: C 39.94; H 4.79; N 8.63. $C_{11}H_{15}O_3N_2Cl_3$. Calculated %: C 40.06; H 4,69 N 8.50.

c) D- and L-threo-I Reduction. 15 g of D- or L-threo-I in 180 ml of alcohol was hydrogenated in the presence of 7.5 g of nickel catalyst base at normal pressure and 18-20°. Reduction was stopped after absorption of one-half of the theoretical volume of hydrogen. The solution was filtered, evaporated in vacuo at 20-25° to a volume of 50 ml, and then an alcoholic solution of HCl added to it. A crystalline precipitate resulted upon gradual addition of ether (200 ml), which was filtered off and washed with alcohol-ether mixture. 5.5-6.0 g (36-39%) of D- or of L-threo-X hydrochloride resulted. The mother liquor was evaporated in vacuo to a small volume, diluted with water and extracted with ethyl acetate. The extract was dried with Na_2SO_4 and evaporated in vacuo. The residue was stirred with ethyl acetate and filtered. 3.5-4.0 g (23-27%) of initial nitro compound (I) resulted, with m.p. 150-151° (from water).

7. Diazotization of D- and L-threo-1-(p-Aminophenyl)-2-dichloroacetylamino-1,3-propandiols (X) and Replacement of the Diazo Group of Diazonium (XI) Salts

a) D- and L-threo-XI (Y = Cl) Synthesis. 3 g of D- or L-threo-X hydrochloride was dissolved in 16.5 ml of 5% HCl and diazotized at 0° with 0.63 g of $NaNO_2$ solution in 3 ml of water. The resulting diazonium salt precipitate was filtered off, washed with water, and dried. Yield was 1.35 g (44%). Upon heating, the substance decomposed without melting.

D-threo-XI (Y = Cl): $[\alpha]_D^{19}$ + 9.5° (c 5.1 in 1% HCl). L-threo-XI (Y = Cl): $[\alpha]_D^{17}$ −9.8° (c 5.1 in 1% HCl). Found %: Cl^- 10.38. $[C_{11}H_{12}O_3N_3Cl_2]^+Cl^-$. Calculated %: Cl^- 10.41.

b) L-threo-VIII (X = Cl) Synthesis. 1 g of L-threo-X hydrochloride was dissolved in 15 ml of 5% HCl and was diazotized at 0-5° with 0.21 g of $NaNO_2$ solution in 1 ml of water. The diazonium salt was added with stirring to Cu_2Cl_2 solution (prepared from 4 g of $CuSO_4 \cdot 5H_2O$ [10]) in 15 ml of 28% HCl, precooled to −5°. After completion of the diazo compound decomposition, the reaction mixture was extracted with ethyl acetate (3 times in 10 ml portions). The extract was washed with water, dried with Na_2SO_4, and evaporated in vacuo. The residue was dissolved in dichloroethane and heptane gradually added to the solution, whereupon resins first isolated were filtered off, and the L-threo-VIII (X = Cl) then precipitated out. Yield was 0.43 g (45%). After recrystallization from water in the presence of charcoal, the m.p. was 92-93°. The substance did not give depression in melting point when mixed with L-threo-VIII (X = Cl) which was synthesized according to Scheme 1.

c) Synthesis of D- and of L-threo-VIII (X = OH). 3 g of D- or of L-threo-X hydrochloride was dissolved in 30 ml of water, 9 ml of 10% H_2SO_4 added, and if needed, the solution was clarified in the cold with charcoal and then diazotized at 0-5° with 0.66 g of $NaNO_2$ solution in 3 ml of water. The HNO_2 excess was decomposed with urea. The diazo solution was then neutralized with $NaHCO_3$ to a pH of 5.5 and then heated at 70-90° to the complete decomposition of diazonium salt. The solution was filtered, heated with carbon, and extracted with ethyl acetate. The extract was dried with Na_2SO_4 and evaporated in vacuo. The residue was stirred with ethyl acetate, filtered off, and recrystallized from ethyl acetate. Yield was 1.4 g (52%).

D-threo-VIII (X = OH): m.p. 160-161° (with decomposition); $[\alpha]_D^{19} - 8.1°$ (c 7.8 in CH_3OH). L-threo-VIII (X = OH): m.p. 160-161° (with decomposition); $[\alpha]_D^{19} + 7.8°$ (c 10.9 in CH_3OH). Found %: N 91; Cl 23.96. $C_{11}H_{13}O_4NCl_2$. Calculated %: N 4.76; Cl 24.13. D,L-threo-VIII (X = OH): m.p. 138-140° (this compound having been prepared from D- and L-threo-VIII (X = OH) by mixing them and subsequently recrystallizing from ethyl acetate).

d) D- and L-threo-VIII (X = CN) Synthesis. 5 g of D- or of L-threo-X was dissolved in 50 ml of water, 15 ml of 10% H_2SO_4 then added, and the solution diazotized at 0-5° with 1.1 g of $NaNO_2$ solution in 4 ml of water. The diazo solution was neutralized with $NaHCO_3$ to a pH of 6.5-7.0, and gradually, with stirring, it was added to a solution of cuprous cyanide under a toluene layer (25 ml) and precooled to −7°.* After completion of diazonium salt decomposition, the reaction mixture was stirred for another 10 minutes and extracted with ethyl acetate (5 times in 40 ml portions). The extract was dried with Na_2SO_4, evaporated to dryness in vacuo, and treated with boiling water (4 times with 50 ml portions). The aqueous solution was heated with charcoal and evaporated in vacuo to 35-40 ml volume. After cooling, there resulted almost pure nitrile. A small amount of substance was again isolated after evaporation of the mother liquor. Yield was 2.4 g (52%). The resulting nitrile was recrystallized with water.

D-threo-VIII (X = CN): m.p. 135.5-136.5°; $[\alpha]_D^{22} + 15.4°$ (c 17.9 in CH_3OH). L-threo-VIII (X = CN): m.p. 135.5-136.5°; $[\alpha]_D^{20} - 17.0°$ (c 8.7 in CH_3OH). Found %: C 47.81; H 4.05; N 9.25. $C_{12}H_{12}O_3N_2Cl_2$. Calculated %: C 47.54; H 4.00; N 9.24. D,L-threo-VIII (X = CN): m.p. 132.5-133.5° (this compound having been prepared from D- and L-threo-VIII (X = CN) by mixing them and subsequently crystallizing them from water).

0.3 g of L-threo-VIII (X = CN) was hydrolyzed under conditions of Experiment 4c. 0.16 g (76%) of L-threo-VII (X = COOH) was isolated, identical with the substance obtained in Experiment 4 c.

e) D- and L-threo-VIII (X = AsO_3H_2) Synthesis. 7 g of the hydrochloride of D- or of L-threo-X was dissolved in 230 ml of 1.5% H_2SO_4, and when needed, the solution was clarified with charcoal in the cold and diazotized at 0-5° with 1.6 g of $NaNO_2$ solution in 5 ml of water. The excess HNO_2 was decomposed with urea and the diazo solution was added over a period of 2 hours, dropwise, to a stirred solution of 0.12 g of $CuSO_4 \cdot 5H_2O$, 2.75 g of As_2O_3 and 5.5 g of Na_2CO_3 in 25 ml of water at 15°. The reaction mixture was stirred for another hour, filtered, acidified with concentrated HCl to a pH of 6.5, evaporated in vacuo, and then filtered again. The filtrate (7-10 ml) was gradually acidified with concentrated HCl to an acid reaction with Congo red, whereupon resins first separated which were filtered off. After addition of ethyl acetate to the solution, at the boundary layer gradual formation of crystals took place. After 10-12 hours, the precipitate was filtered off, washed with ethyl acetate and dried. The dry substance was heated with 15 ml of alcohol, the solution filtered, and evaporated to dryness in vacuo. The residue was mixed with ethyl acetate and the precipitate filtered off. Weight was 2.2 g. The substance was dissolved in 2 times the volume of hot absolute alcohol and precipitated with ethyl acetate, whereupon a crude product first separated, and then the pure arsonic acid. Yield was 1.36 g (16%). The substance did not possess a sharp melting point.

D-threo-VIII (X = AsO_3H_2): $[\alpha]_D^{20} + 8.6°$ (c 7.8 in CH_3OH). L-threo-VIII (X = AsO_3H_2): $[\alpha]_D^{22} - 7.8°$ (c 7.9 in CH_3OH). Found %: As 18.09; N 2.91. $C_{11}H_{14}O_6NCl_2As$. Calculated %: As 18.64; N 3.48.

f) D- and L-threo-VIII [X = 3,4-$(NO_2)(HO)C_6H_3N = N-$.] Synthesis. 6 g of D- or of L-threo-X hydrochloride was dissolved in 80 ml of 2.5% HCl, clarifying if necessary in the cold with charcoal, and diazotized at 0 to −5° with 1.4 g of $NaNO_2$ solution in 7 ml of water. Excess HNO_2 was decomposed with urea. The diazo solution was poured into 2.8 g of o-nitrophenol, 7.3 g of NaOH and 3.5 g of Na_2CO_3 dissolved in 65 ml of water at 0 to −5°, and stirred at 15-20° for 2 hours, and acidified with 5% HCl to an acid Congo red reaction. After standing for 12 hours at 0 to −5°, the resulting resinous substance solidified, was stirred, washed with water, and dried. The azo compound was extracted repeatedly with boiling dichloroethane and was precipitated with double the volume of heptane, after which it was recrystallized from 30% CH_3COOH. Yield was 2.3 g (29%).

D-threo-VIII [X = 3,4-$(NO_2)(HO)C_6H_3N = N-$]: m.p. 157-159°; $[\alpha]_D^{22} + 21.2°$ (c 5.3 in CH_3OH). L-threo-VIII [X = 3,4-$(NO_2)(HO)C_6H_3N = N-$]: m.p. 157-159°; $[\alpha]_D^{16} - 22.0°$ (c 7.5 in CH_3OH). Found %: N 12.33. $C_{17}H_{16}O_6N_4Cl_2$. Calculated %: N 12.64. D,L-threo-VIII [X = 3,4-$(NO_2)(HO)C_6H_3N = N-$]: m.p. 153-155° (this compound was prepared from D- and L-threo-VIII [X = 3,4-$(NO_2)(HO)C_6H_3N = N-$] by combining them, followed by their recrystallization from dichloroethane).

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* The latter was obtained by mixing 10 g of KCN solution in 20 ml of water with Cu_2Cl_2 suspension (from 12 g of $CuSO_4 \cdot 5H_2O$ [10]) in 20 ml of water, and neutralizing the resulting solution with a 10% solution of CH_3COOH to a pH of 7.0-7.5.

8. Condensation of D- and of L-threo-1-(p-Aminophenyl)-2-dichloroacetyalmino-1,3-propandiols (X) with p-Nitronitrosobenzene and p-Nitrobenzaldehyde

a) D- and L-threo-VIII (X = p-$NO_2C_6H_4N$ = N−) Synthesis. 2.3 g of D- or of L-threo-X hydrochloride solution in 15 ml of methanol was mixed with 0.8 g anhydrous CH_3COONa in 10 ml of methanol, filtered, cooled to 5° and a solution of 0.95 g of p-nitronitrosobenzene in 15 ml of CH_3COOH added. After 10-12 hours, the resulting crystals of p,p'-dinitroazoxybenzene were filtered: weight 0.13 g, m.p. 191-192° (from CH_3COOH) [11]. The filtrate was evaporated in vacuo, the residue stirred with benzene, filtered off, washed with methanol and crystallized from ethyl alcohol. Yield was 1.48 g (56%).

D-threo-VIII (X = p-$NO_2C_6H_4N$ = N−): m.p. 173-174°; $[\alpha]_D^{20}$ −62.2° (c 0.6 in acetone). L-threo-VIII (X = p-$NO_2C_6H_4N$ = N−): m.p. 173-174°; $[\alpha]_D^{20}$ + 64.9° (c 0.8 in acetone). Found %: C 48.04; H 3.39; N 13.30. $C_{17}H_{16}O_5N_4Cl_2$. Calculated %: C 47.79; H 3.77; N 13.11. D,L-threo-VIII (X = p-$NO_2C_6H_4N$ = N−): m.p. 171-172° (this compound having been prepared from D- and from L-threo-VIII (X = p-$NO_2C_6H_4N$ = N−) by mixing them and recrystallizing from alcohol.

b) D- and L-threo-VIII (X = p-$NO_2C_6H_4CH$ = N−) Synthesis. 2 g of D- or of L-threo-X hydrochloride and 0.9 g of p-nitrobenzaldehyde were dissolved in 25 ml of methanol and mixed with a solution of 1.2 g of CH_3COOK (anhydrous) in 25 ml of methanol. The reaction mixture was left for 1 hour at 15-20°, was then heated to boiling, 95 ml of hot water added to it, and the solution heated with charcoal. After cooling, the resulting precipitate was filtered off, washed with methanol and dried. Yield was 1.6 g (62%). The substance was recrystallized from ethyl alcohol.

D-threo-VIII (X = p-$NO_2C_6H_4CH$ = N−): m.p. 164-166° with decomposition; $[\alpha]_D^{20}$ −18.8° (c 3.6 in dioxane). L-threo-VIII (X = p-$NO_2C_6H_4CH$ = N−): m.p. 165-167° with decomposition; $[\alpha]_D^{20}$ + 19.7° (c 2.5 in dioxane). Found %: C 50.62; H 4.01; N 9.75. $C_{18}H_{17}O_5N_3Cl_2$. Calculated %: C 50.72; H 4.03; N 9.85. D,L-threo-VIII (X = p-$NO_2C_6H_4CH$ = N−): m.p. 155-157° with decomposition. (This compound was obtained from D- and L-threo-VIII (X = p-$NO_2C_6H_4CH$ = N−) by combining them, followed by recrystallization from alcohol).

SUMMARY

Two general synthetic methods have been developed for optically-active chloromycetin (levomycetin) analogs of the type:

$$p\text{-}XC_6H_4CHOHCH(NHCOCHCl_2)CH_2OH.$$

Both methods of synthesis make it possible to start with compounds of known steric configuration which do not change during the process of synthesizing the analogs indicated.

By these procedures, chloromycetin analogues of the D- and L-threo-series, which have X = Cl, I, OH, CN, COOH, AsO_3H_2, 4-$NO_2C_6H_4CH$ = N−, 4-$NO_2C_6H_4N$ = N− and 3,4-$(NO_2)(HO)C_6H_3N$ = N−, have been synthesized.

The synthetic procedures which have been developed may be used to prove the steric structures of certain types of chloromycetin analogs obtained by the methods of other investigators and which are described in the literature. It has been demonstrated that the method of Long and Troutman, published previously, leads, in a number of cases, to chloromycetin analogs belonging to the threo-series.

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RESEARCH IN THE FIELD OF CONJUGATED SYSTEMS

LII. CONCERNING THE SEQUENCE OF BROMINE ADDITION TO VINYLALKYLACETYLENES

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Compounds with conjugated double and triple bonds (eninic systems) possess a number of specific peculiariti which distinguish them from compounds containing conjugated double bonds.

The simplest member of the eninic systems −vinylacetylene− is capable of a hydrogen atom replacement by metals, and of various condensations at the expense of this hydrogen, as well as of addition reactions of water, alcohols and acids (under conditions of the Kucherov reaction) at the acetylenic bond [1]. None of these reactions is characteristic for divinyl. On the other hand, vinylacetylene, in contrast to divinyl, almost fails to enter into homo- and hetero-cyclization reactions (dienic syntheses), apparently because of steric hindrances (linear placement of the three carbon atoms). Similar distinctions can also occur with homologs of these two hydrocarbons.

The vinylacetylene addition reaction attests to the high reactivity of the first carbon atom in the molecule. Hydrogen halides add to it in the 1,4-position, with formation of the allene halogenides which, under influence of catalysts, readily rearrange to diene halogenides (allene-dienic isomerization with change in the halogen position). The latter substances are formed directly as the result of addition of hydrogen halides in the presence of catalyst which promotes the isomerization[2].

As experiments by one of us with Sopov [3] have demonstrated, bromine adds to vinylacetylene chiefly at the 1,2-, but also at the 1,4-position. 1,4-Dibromide is capable of rearrangement to 1,2-dibromide with conjugated double bonds, in the presence of catalysts. Among the products of this reaction a third isomer was also present −acetylene dibromide, but its amount was quite small.

According to the literature data, vinylacetylene homologs with a radical in the first position behave analogously to vinylacetylene. Thus, an investigation of their reaction with hydrogen chloride did not evidence any peculiarities as compared with vinylacetylene [4].

The experiments set up for bromination of vinylalkylacetylenes led to unexpected results: bromine addition took place almost exclusively at the double bond (3,4-position).

It might be expected that the following three dibromides (I), (II) and (III) would be formed from the addition of bromine to vinylacetylene homologs

$$\underset{(I)}{R{-}CBr{=}CBr{-}CH{=}CH_2};\qquad \underset{(II)}{R{-}C{\equiv}C{-}CHBr{-}CH_2Br};\qquad \underset{(III)}{R{-}CBr{=}C{=}CH{-}CH_2Br.}$$

In actuality, substances with very narrow boiling range resulted, having the following properties:

1) Upon oxidation with permanganate and by ozonization, they form α,β-dibromopropionic acid, along with the corresponding carboxylic acid from the second part of the molecule (the first homolog giving acetic acid, and the second propionic acid). With ozonization, only one molecule of ozone is absorbed. The ozonization rate curve does not possess inflexions, which indicates the presence of only one multiple bond (see Figure).

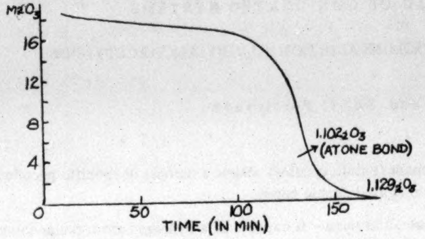
2) Upon reaction with alcoholic alkali in the cold, they immediately split out one hydrogen bromide molecule, with formation of the monobromides of the vinylacetylene series.

3) When stored for several months, they do not polymerize.

4) When reacted with Cu_2Br_2 + HBr, they convert readily to dienic dibromides, stable to alkali, and polymerizing upon storage, exposure to light, and with heating.

5) 2240 cm^{-1} (intense) and 2347 cm^{-1} (faint) are found for the combined dispersion spectrum of dibromide prepared from hexenine, which are characteristic for a triple bond between the 2 and 3 carbon atoms. In the spectrum for its isomerization product −diene dibromide− there is found an intense frequency at 1611 cm^{-1} for the double bond. There are no frequencies for the triple bond.

None of these properties coincides with Formulas (I) or (III), which makes it possible to ascribe, without hesitation, Formula (II) to the dibromides obtained.



Along with the main fraction of dibromides, there usually results in addition lower fractions; however, their amount is small and does not constitute more than 10% of the main fraction. Apparently diene dibromides are contained in these lower fractions, since they give a high refractive index and upon storage resinify readily.

The residue from distillation of the dibromides contains tetrabromides. The latter were not isolated in pure state: they decompose somewhat upon distillation in vacuo.

The acetylene dibromides (II) were slightly yellow liquids with a pine odor, somewhat irritating. They possessed slightly higher boiling points as compared with the corresponding halogen derivatives (1,2-dibromopentane had a b.p. of 68°, 1,2-dibromohexane 82°, 1,2-dibromoheptane 98-99° at 12 mm, 1,2-dibromooctane 118.5° at 15 mm). With increase in alkyl, this difference decreases somewhat. For all of the dibromides the molecular refraction values found are higher than calculated. This phenomenon exists for other unsaturated bromides of the allyl type. Within a homologous series of dibromides, specific gravity decreases and refractive index decreases, according to the rule. The most important constants for acetylene dibromides are given in Table 1.

TABLE 1

Substance	Boiling point at 10 mm (in °)	d_4^{20}	n_D^{20}	MR_D	
				Found	Calculated
$CH_2Br-CHBr-C\equiv C-CH_3$	79.5-80.5	1.8300	1.5588	39.85	38.82
$CH_2Br-CHBr-C\equiv C-C_2H_5$	87-87.5	1.6920	1.5470	44.98	43.44
$CH_2Br-CHBr-C\equiv C-C_3H_7$	100-102	1.6008	1.5348	49.38	48.05
$CH_2Br-CHBr-C\equiv C-C_4H_9$	114-115	1.5191	1.5300	54.50	52.67
$CH_2Br-CHBr-C\equiv C-C_5H_{11}$-iso	121-123	1.4590	1.5238	59.13	57.29
$CH_2=CH-CBr=CBr-CH_3$	57-57.5	1.8304	1.5768	40.89	39.89
$CH_2=CH-CBr=CBr-C_2H_5$	69.5-70	1.7089	1.5640	45.67	44.50
$CH_2=CH-CBr=CBr-C_3H_7$	85.5-86	1.6075	1.5518	50.47	49.12
$CH_2=CH-CBr=CBr-C_4H_9$	101.5-102.5	1.5319	1.5440	55.23	53.74
$CH_2=CH-CBr=CBr-C_5H_{11}$-iso	111-113	1.4614	1.5330	59.88	58.36

Diene dibromides with a conjugated double bond system differ from the acetylene dibromides in a considerably lower boiling point, by higher refractive index, but differ very little in specific gravity. All of these compounds possess high values for molecular refraction and show exaltation. In contrast to acetylene dibromides, the diene dibromides possess quite a pleasant odor. Upon storage they become brownish and polymerize. In an open container, and in small mass, polymerization is in process within a matter of days. Standard inhibitors cut down polymerization. When mixed with alcoholic alkali in the cold, these compounds do not change significantly.

The products of hydrogen bromide rupture from acetylene dibromides are colorless liquids with sharp, persistent odor, characteristic for halogenated acetylene derivatives. Upon storage, and even in the presence of inhibitors, they convert rapidly (after 2-3 days) into a dark-colored resin. Non-reactive with ammoniacal silver oxide solution. Constants are given in Table 2.

It can be seen from Table 2 that for a homologous series there occurs an increase in boiling point according to the rule, and a decrease in specific gravity and refractive index. All of the compounds exhibit considerable molecular exaltation (1.2-1.8).

The authors attempted to obtain the diene tribromide $CH_2=CBr-CBr=CBr-C_2H_5$ by reacting hexenine tetrabromide with alcoholic alkali. The resulting substance boiled over a wide temperature range, and contained a somewhat lower bromine percentage than would be required according to theory. Evidently, the reaction of tetrabromide with alkali proceeds with formation of a mixture of these two substances.

TABLE 2

Substance	Boiling point at 40 mm (in °)	d_4^{20}	n_D^{20}	MR_D	
				Found	Calculated
$CH_2=CBr-C\equiv C-CH_3$	52-53	1.4010	1.5255	31.75	30.59
$CH_2=CBr-C\equiv C-C_2H_5$	67.5-68.5	1.3081	1.5156	36.70	35.20
$CH_2=CBr-C\equiv C-C_3H_7$	83-84	1.2443	1.5092	41.58	39.82
$CH_2=CBr-C\equiv C-C_4H_9$	102-103	1.2005	1.5051	46.24	44.44
$CH_2=CBr-C\equiv C-C_5H_{11}$-iso	113-115	1.1619	1.4998	50.89	49.08

It was thus established that vinylacetylene homologs with a radical in the first position, add bromine predominately at the ethylene bond. The double bond is found to be more reactive, compared to the triple bond. There is no conjugation.

This peculiarity in the addition reaction of vinylacetylene homologs is evidently related to the fact that under the influence of the radicals, electrons of the conjugated system are strongly displaced to the double bond side, and in addition, entrance of bromine into the first position meets with steric hindrance. Of considerable significance is also a decreased tendency for the vinylacetylene system to undergo addition reactions at the 1,4-position, because of peculiarity in their configuration, as was mentioned at the beginning of this article. It is possible that relative stability of the 3,4-product under conditions of the bromine addition reaction is of significance.

EXPERIMENTAL

The vinylalkylacetylenes required for the investigations were prepared according to standard procedures, in yields of 35 to 80% [4]. The yield increased with increase in molecular weight of the alkyl group.

1. Bromination of Vinylalkylacetylenes

Penten -1-ine-3. 53 g (17 ml) of bromine in 100 ml of chloroform was added, over a period of 5 hours, with strong mechanical stirring and cooling to −8° to −10°, to a solution of 43 g of the hydrocarbon (double excess) in 250 ml of chloroform.

After completion of reaction, the chloroform and unreacted hydrocarbon were distilled on a water bath at low pressure, and the residue distilled in vacuo at 10 mm. The chloroform solution of hydrocarbon was again brominated with half the original volume of bromine. The reaction products were separated by the above-indicated method, and the original fraction brominated for a third time. Thus was achieved almost complete utilization of the hydrocarbon, maintaining in twice the amount relative to bromine. About 120 g of bromides was obtained from 100 g of bromine. The fractions resulting from distillation at 10 mm were as follows: 1st, 60-70° 3.8 g; 2nd, 70-79.5° 6.0 g; 3rd, 79.5-80.5° 76 g; 4th, 80.5-100° 2.5 g; 5th, 100-132° 4.4 g; 6th, 132-136° 24.5 g; 7th, 136-145 4.4 g; 8th, residue 5.0 g. With the fractions distilling above 100°, there was observed a little decomposition.

Constants for the principal fractions are given in Table 1, analytical data in Table 3. The following frequencies were observed in the combined dispersion spectrum 2347 cm^{-1} (weak), 2240 (very strong), 1612 (indistinct), 1372, 1232, 1157, 1117, 1011 (weak), 711 (average), 669 (very strong). The first two frequencies may belong just to the triple bond. The appearance of 1612 cm^{-1} is related to isomerization of acetylene dibromide into the diene dibromide by exposure to light. Actually, after exposure to light (for 4 hours), the substance upon distillation gives a lower fraction, corresponding to the diene dibromide, and exhibiting a higher refractive index as compared with the original (n_D^{20} 1.5626). The last two frequencies belong to the C−Br bonds.

The main fraction of 5.19 g was ozonized in chloroform.* 1.129 g of ozone was absorbed (for one bond, 1.102 g was required), and ozonization was then terminated. The ozonization rate curve is given in the Figure. After decomposition of the ozonides with 2% H_2O_2, 0.9 g of acetic acid and 2.7 g of acids with b.p. 130-135° at 10 mm were extracted with ether from the solutions. Acetic acid was converted into the anilide, with m.p. 113°, which corresponded with the literature data [5]. Upon cooling, about 1.1 g of α,β-dibromopropionic acid, with m.p. 64-66°, was isolated from the above-boiling acids. A mixture of the substance with known α,β-dibromopropionic acid (prepared by bromination of acrylic acid in chloroform) had the same melting point.

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* The authors wish to express their appreciation to A. I. Yakubchik and to N. G. Kasatkina for investigation of the ozonization rate.

0.1024 g sub.: 0.1653 g AgBr. Found %: Br 68.69. $C_3H_4O_2Br_2$. Calculated %: Br 68.77.

7 g of dibromide was oxidized with potassium permanganate (dry permanganate being added in small portions to the vigorously-stirred dibromide mixture, with 100 ml of water and 12 g of $MgSO_4 \cdot 7H_2O$, 11.8 g of permanganate being used). After standard treatment of the reaction mixture, 0.8 g of acetic acid and about 0.8 g of crystalline α,β-dibromopropionic acid, with m.p. 62-64° resulted (after washing the resulting crystals with petroleum ether).

For the 132-136° fraction at 10 mm, there were found: d_4^{20} 2.3496; n_D^{20} 1.6160.

0.1929 g sub.: 0.3623 g AgBr. Found %: Br 79.92. $C_5H_6Br_4$. Calculated %: Br 82.93.

The analytical data indicate that the fraction was the tetrabromide of the original hydrocarbon, which decomposed somewhat upon distillation (with splitting out of hydrogen bromide).

Hexen -1-ine-3. 52 g of bromides was obtained from 20 g of hydrocarbon and 37 g of bromine under the above-indicated conditions.

Fractions resulting from distillation at 10 mm: 1st, 70-80° 2 g; 2nd, 80-85° 1.8 g; 3rd, 85-90° 21.8 g; 4th, 90-95° 2 g; 5th, 95-100° 1.5 g; 6th, 100-140° 2 g; 7th, 140-150° 10 g; 8th, residue 4.6 g.

Constants for the major fractions are given in Table 1, the analytical data in Table 3. First fraction had n_D^{20} 1.5544.

6 g of the substance was ozonized. After standard treatment of the ozonide, 1.2 g of propionic acid and 3.5 g of acids distilling in the range 125-135° at 10 mm resulted. The propionic acid was identified as the anilide with m.p. 104°. Crystalline α,β-dibromopropionic acid (m.p. 62-64°) was isolated from the higher fraction.

The sixth fraction was the tetrabromide of the initial hydrocarbon which decomposed somewhat during the distillation. For it there were found: d_4^{20} 2.2035; n_D^{20} 1.6020.

0.1476 g sub.: 0.2728 g AgBr. Found %: Br 78.65. $C_6H_8Br_4$. Calculated %: Br 79.96.

Hepten -1-ine-3. 105 g of bromides resulted from 42 g of hydrocarbon and 71 g of bromine. The substance was separated into the following fractions as the result of distillation: 1st, to 94° 3.4 g; 2nd, 94-99° 3.6 g; 3rd, 99-104° 60.1 g; 4th, 104-110° 6.0 g; 5th, residue 27 g. In this case, and in subsequent cases, constants for the principal fractions are given in Table 1, analytical data in Table 3.

Octen -2-ine-3. 109 g of bromides resulted from 54 g of hydrocarbon and 70 g of bromine. Distillation at 10 mm gave the following fractions: 1st, 107-110° 1.8 g; 2nd, 110-116° 67 g; 3rd, 116-122° 4.2 g; 4th, residue 32.8 g.

7-Methylocten —1-ine-3. 85 g of bromides resulted from 45 g of hydrocarbon and 53 g of bromine. Distillation at 10 mm yielded the following fractions: 1st, 117-122° 1.5 g; 2nd, 122-126° 45.5 g; 3rd, 126-130° 4.5 g; 4th, residue 28 g.

2. Isomerization of Acetylene Dibromides into Diene Bromides

0.1 mole of acetylene dibromide was dissolved in 50 ml of ether and heated under reflux on a water bath with 50 ml of 48% hydrobromic acid and 10 g of Cu_2Br_2 for 4-6 hours. The mixture was then diluted with water, the ether layer separated, and the residue extracted with ether. The ether solutions of dibromide were washed with water, dried with $CaCl_2$ and distilled: ether was distilled off at normal pressure, the residue distilled in vacuo. Here the main fraction went over within a range of 0.5-1°, the yield of this fraction constituting about 70-80% of the total material. Constants for the diene dibromides are given in Table 2, and the analytical data in Table 3.

The relationship between diene dibromides and alcoholic alkali was studied under the following conditions: a weighed sample (about 1 g) was added in the cold to 15% ethanolic solution of KOH, and after a lapse of 4-5 hours the amount of bromide ion determined in the solution. The first member of the diene dibromide series in this case lost 5% bromine, and the second 6%.

The following frequencies were found in the combined dispersion spectrum: 143, 172, 214 (weak), 460, 510, 917, 956 (average), 1160 (strong), 1257, 1295, 1403 (average), 1517 (weak), 1611 (very strong), 2932, 2977, 3029 (weak) cm^{-1}.*

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* The authors wish to express their appreciation to T. V. Yakovleva for assistance in measuring the spectra.

TABLE 3

Substance	Sample weight (in g)	AgBr (in g)	% Br	
			Found	Calculated
$CH_2Br-CHBr-C\equiv C-CH_3$	0.1576	0.2595	70.08	70.74
$CH_2Br-CHBr-C\equiv C-C_2H_5$	0.1356	0.2120	62.52	66.61
$CH_2Br-CHBr-C\equiv C-C_3H_7$	0.1393	0.2026	63.11	62.93
$CH_2Br-CHBr-C\equiv C-C_4H_9$	0.1572	0.2168	58.68	59.64
$CH_2Br-CHBr-C\equiv C-C_5H_{11}$-iso	0.1769	0.2365	56.89	56.67
$CH_2{=}CH-CBr{=}CBr-CH_3$	0.1900	0.3130	70.09	70.74
$CH_2{=}CH-CBr{=}CBr-C_2H_5$	0.1908	0.2962	66.06	66.61
$CH_2{=}CH-CBr{=}CBr-C_3H_7$	0.1760	0.2604	62.96	62.93
$CH_2{=}CH-CBr{=}CBr-C_4H_9$	0.1186	0.1650	59.20	59.64
$CH_2{=}CH-CBr{=}CBr-C_5H_{11}$-iso	0.1083	0.1440	56.58	56.67
$CH_2{=}CBr-C\equiv C-CH_3$	0.1348	0.1744	55.05	55.11
$CH_2{=}CBr-C\equiv C-C_2H_5$	0.1532	0.1804	50.10	50.25
$CH_2{=}CBr-C\equiv C-C_3H_7$	0.1218	0.1312	45.83	46.18
$CH_2{=}CBr-C\equiv C-C_4H_9$	0.1347	0.1352	42.71	42.71
$CH_2{=}CBr-C\equiv C-C_5H_{11}$-iso	0.1482	0.1373	39.40	39.74

3. Synthesis of Monobromovinylacetylenes

Upon treating acetylene dibromides in the cold with a slight excess of 15% alcoholic KOH, exactly one-half of the bromine contained in the compound is split off in the form of bromide ion Thus, a 7.2 g batch of the first homolog lost in this case 2.55 g of bromine in the form of bromide ion, which constituted 50.06% (7.2 g), and of the second homologs 2.36 g of bromine, which constituted 49.2%, analogous data for the third and fourth homologs being 48.8 and 48.0%.

After dilution of the reaction mixture with water, the reaction products were distilled with steam. Yield of bromovinylacetylene amounted to 55-60%. Their constants are given in Table 2, the analytical data in Table 3.

4. Reaction of Alcoholic Alkali With Hexenine Tetrabromide

2.2 g of KOH in alcoholic 10% solution was added to 12.8 g of tetrabromide, with stirring and cooling. Potassium bromide precipitated immediately. An oil separated from the reaction mixture upon dilution with water, which, after washing with water, and drying over $CaCl_2$, was distilled in vacuo at 10 mm. The following fractions resulted: 1st, to 116° 2 g; 2nd, 116-121° 4.2 g; 3rd, above 121° 2 g.

For the 116-121° fraction at 10 mm: d_4^{20} 1.9744; n_D^{20} 1.5935.

0.1520, 0.1762 g sub.: 0.2627, 0.3028 g AgBr. Found %: Br 73.55, 73.13. $C_6H_7Br_3$. Calculated %: Br 75.19.

SUMMARY

1. The sequence of bromine addition to vinylalkylacetylenes has been investigated. It has been established that, in contrast to vinylacetylene, homologs of the indicated type add bromine chiefly at the double bond. The structure of the reaction products has been proved by ozonization and by oxidation, as the result of which there are formed α,β-dibromopropionic acid and the corresponding unsubstituted carboxylic acids.

2. Upon reacting Cu_2Br_2 with acetylenic dibromides, there have been obtained diene dibromides which differ considerably, by lower boiling points, stability to alkali, and tendency to polymerize.

3. A series of monobromovinylacetylenes has resulted from reaction of acetylene dibromides with alcoholic alkali.

4. Peculiarities of reaction for vinylacetylene homologs relative to bromine have been explained on the assumption of molecular rearrangement of these substances under the influence of a reactive radical center on one side of the double bond, as well as conditions of steric hindrance to the addition reaction.

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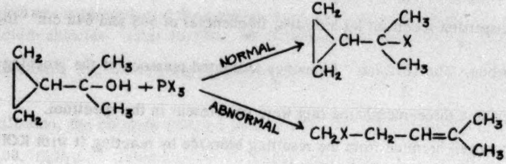
* See Consultants Bureau Translation, page 745.

REACTION OF PHOSPHORUS TRICHLORIDE AND OF TRIBROMIDE WITH DIMETHYLCYCLOPROPYLCARBINOL

Ya. M. Slobodin, V. I. Grigoryeva and Ya. E. Shmulyakovsky

It was demonstrated in the works by one of us [1, 2] that interaction of methylcyclopropylcarbinol with phosphorus halides proceeds "abnormally", as the result of which there are formed unsaturated halogen derivatives with an open chain of carbon atoms. It has been established that the degree to which a three-membered ring is opened up depends upon the nature of the halogen atom. If iodine causes complete opening of the ring [3], then bromine does not open it completely (70%) and chlorine causes opening only on a small scale (10%) [1]. The introduction of two chlorine atoms into the α-position of a three-membered ring leads to formation of an "abnormal" reaction product to the same degree as does one bromine atom (70%).

It was of interest to study the interaction of dimethylcyclopropylcarbinol with PCl_3 and PBr_3.



Considering the tertiary character of carbinol, ring opening on a larger scale than in the case of methylcyclopropylcarbinol might be expected.

Bruylants [4], by reacting dimethylcyclopropylcarbinol with hydrogen bromide, obtained a bromide to which he attributed the cyclic structure. Upon splitting out hydrogen bromide, there resulted a hydrocarbon which was accepted by the authors as isopropenylcyclopropane; however, from its properties, this hydrocarbon was found to be identical with 2-methylpentadiene-2,4. It should be considered that the bromide obtained by Bruylants also possessed an open chain of carbon atoms.

In a study of the reaction of hydrogen chloride with the same carbinol, Bruylants prepared the chloride, to which he at first also attributed the cyclic structure. Later, the structure, 5-chloro-2-methylpentane-2, was attributed to this chloride [5].

T. A. Favorskaya [6-9], who studied in detail the properties and the conversion of tertiary alcohols of the cyclopropane series, proved that upon interacting dimethylcyclopropylcarbinol with hydrochloric acid there is indeed formed an unsaturated primary monochloride with an open chain of carbon atoms. A dichloride was formed as a secondary product.

In the present investigation, interaction of dimethylcyclopropylcarbinol with PCl_3 and PBr_3 has been studied.

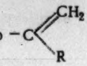
After fractionation of the interaction products of carbinol with PCl_3, the chloride was isolated in yield 45% of theory. In addition, a hydrocarbon was obtained, which resulted from spontaneous splitting out of hydrogen chloride.

In its properties the chloride hardly differed from chlorides that were obtained by Bruylants and Favorskaya by reacting carbinol with hydrochloric acid.

Frequencies of 655 and 718 cm^{-1} in the combined dispersion spectrum of the chlorides indicated presence of a chlorine atom on a primary carbon, and the intense line with a frequency of 1673 cm^{-1}, presence of the group $-HC=C\langle{}^{R}_{R}$. There are group frequencies in the spectrum which definitely indicated the presence of chloride addition which contained a tri-membered ring (877, 924, 1193 cm^{-1}).

With ozonolysis of the chloride, acetone, acetone peroxide and β-chloropropionic acid were isolated. This confirmed that the chief component part of the chloride was 5-chloro-2-methylpentene-2.

The hydrocarbon which was isolated by distillation of the crude chloride was found, from its properties, to be identical with isopropenylcyclopropane.

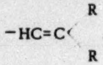
Intense lines with frequencies 895, 968, 1191, 3011, 3081 cm^{-1} were found in the combined dispersion spectrum for this hydrocarbon, which characterized the cyclopropane structure, and a line at the 1648 cm^{-1} frequency, characterizing the group  $-C{<}^{CH_2}_{R}$.

Upon hydrogenation over platinum catalyst, the quantity of hydrogen absorbed corresponded to one double bond.

Thus, upon interacting dimethylcyclopropylcarbinol with PCl_3, both the normal and the abnormal reactions proceeded on the same scale.

By splitting out of hydrogen chloride from 5-chloro-2-methylpentene-2, by reacting with KOH, a diene hydrocarbon resulted, which upon hydrogenation added 2 moles of water. The combined dispersion spectrum for this hydrocarbon, and its properties, corresponded to 2-methylpentadiene-2,4.

Upon reacting dimethylcyclopropylcarbinol with PBr_3, there resulted the bromide in yield of 86% of theory. The hydrocarbon was not found among the reaction products.

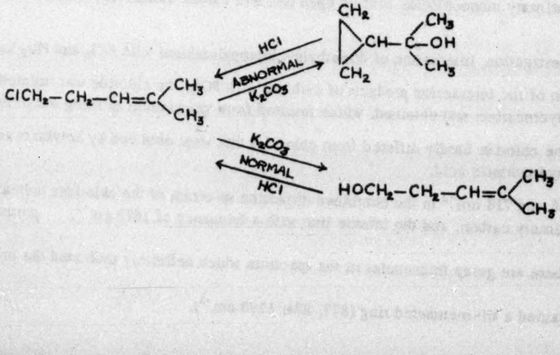
In the combined dispersion spectrum for bromide, frequencies of 563 and 643 cm^{-1} indicated presence of bromine at a primary carbon. The 1672 cm^{-1} frequency indicated presence of the grouping  $-HC{=}C{<}^{R}_{R}$. Frequencies which characterize a three-membered ring were not present in the spectrum.

Upon rupture of hydrogen bromide from the resulting bromide by reacting it with KOH, a hydrocarbon was prepared which was found to be 2-methylpentadiene-2,4.

Thus, the interaction of dimethylcyclopropylcarbinol with PBr_3 leads to formation of the abnormal product only − 5-bromo-2-methylpentene-2.

The works of Bruylants [5] and Favorskaya [7] have established that 5-chloro-2-methylpentene-2 upon saponification with potash converts into dimethylcyclopropylcarbinol. According to Favorskaya's directions, the reaction products contain as impurity an unsaturated compound which does not possess chlorine.

The authors effected saponification of chloride under the conditions given in Favorskaya's work. In the combined dispersion spectrum for the saponification products, all of the frequencies for dimethylcyclopropylcarbinol were found. Along with this fact, there were preserved in the spectrum markedly weakened lines of the initial chloride. Determination of chlorine content indicated that the saponification products contained about 18% of unchanged chloride. Moreover there was found in the spectrum a line of frequency 1674 cm^{-1}, the intensity of which was considerably greater than could be expected from the unsaturated chloride content. This data makes it possible to assume that upon saponification of unsaturated chloride, there is formed, along with the tertiary cyclic carbinol, 2-methylpentene-2-ol-5 − the normal product of chloride saponification.



EXPERIMENTAL

Dimethylcyclopropylcarbinol

The initial acetylcyclopropane was prepared according to the method of Wagner [10] as modified by Slobodin and Shokhor [11].

Dimethylcyclopropylcarbinol was prepared, according to the standard method, from acetylcyclopropane and methyl magnesium iodide. Yield of carbinol was 75% of theory. The carbinol boiled at 122-123°; d_4^{20} 0.8816; n_D^{20} 1.4338; MR_D 29.53. $C_6H_{12}O$. Calculated MR_D 29.94.

Combined dispersion spectrum:

262 (0.5), 278 (0.5), 333 (6), 355 (3), 368 (0.5), 389 (0.5), 405 (0.5), 441 (0.5), 478 (2), 514 (3), 539 (3), 588 (2), 632 (2), 691 (15), 742 (1), 786 (4), 822 (7), 844 (9), 851 (9), 913 (9), 933 (9), 958 (9), 997 (1), 1023 (0.5), 1064 (4w), 1105 (1), 1141 (4), 1172 (4), 1201 (20), 1238 (3), 1364 (2), 1424 (9), 1442 (9), 1467 (9), 2867 (2), 2911 (9), 2930 (9), 2971 (10), 3008 (15), 3073 (4w).

I. Reaction of PCl_3 With Dimethylcyclopropylcarbinol

A few drops of pyridine was added to 20 g of PCl_3 dissolved in 150 ml of dry ether. 40 g of carbinol and 16 g of pyridine as a mixture was added to the mixture gradually through a dropping funnel. The rate of addition was regulated in such a manner that the temperature of the mixture did not exceed 30-35°. After addition of a small amount of the carbinol, the mixture was kept for 0.5 hour at room temperature, after which it was poured into ice water The ether solution was separated, and the aqueous layer extracted with ether. The combined ether solution was dried over calcium chloride. After distilling off the ether, hydrogen chloride evolution was observed.

Isolation of the fractions: 1st, 54-78°, 8 g (hydrocarbon); 2nd, 79-128°, 7 g; 3rd, 129-133°, 20.5 g (chloride).

Upon second distillation, the chloride distilled over at 132-134°; d_4^{20} 0.9164; n_D^{20} 1.4468; MR_D 34.54.

Found %: Cl 31.00. $C_6H_{11}Cl$. Calculated %: Cl 29.96; MR_D 34.32.

Combined dispersion spectrum for the chloride:

261 (6), 375 (0.5), 461 (2), 512 (0.5), 590 (0.5), 655 (10), 718 (10), 751 (8), 777 (0.5), 799 (5), 834 (5), 877 (0.5), 924 (1), 971 (1), 1029 (4), 1070 (3), 1103 (3), 1146 (2), 1193 (1), 1234 (2), 1278 (2), 1316 (4), 1351 (3), 1381 (10), 1445 (10), 1673 (20), 2856 (2), 2911 (5), 2959 (3), 2997 (0.5).

Ozonolysis of the Chloride. 4.2 g of chloride was dissolved in ethyl chloride and ozonized with 3% ozone. The ozonide, after removal of solvent, was decomposed by boiling with water. On cooling, acetone peroxide crystals, m.p. 129°, separated on the walls of the flask. Upon heating on a spatula they exploded. The aqueous solution was distilled. Acetone was found in the fraction boiling up to 100°, according to reaction with 2,4-dinitrophenylhydrazine. The residue in the distilling flask was extracted with ether. After removal of the ether, β-chloropropionic acid with m.p. 38° was isolated.

Saponification of the Chloride. 4 g of the chloride was boiled for 12 hours in a flask equipped with reflux condenser, with 50 ml of 10% potash solution. The reaction products were extracted with ether. The ether solution was dried overnight over sodium sulfate. Upon fractionation, the fraction with m.p. 122-124° was isolated in the amount of 3.2 g; n_D^{20} 1.4341 (dimethylcyclopropylcarbinol n_D^{20} 1.4338).

0.1474, 0.1980 g sub.: 0.0340, 0.0407 g AgCl. Found %: Cl 5.1, 5.7, which recalculated on the chloride content, amounted to about 18%.

Combined dispersion spectrum:

251(1), 278 (1), 333 (2), 392 (0.5), 417 (0.5), 518 (1), 538 (1), 655 (1), 692 (10), 720 (2), 750 (1), 786 (3), 823 (4), 847 (7w), 912 (4), 931 (6), 1000 (0.5), 1013 (1), 1065 (2w), 1106 (1), 1142 (2), 1199 (15), 1238 (2), 1384 (3w), 1448 (8w), 1674 (4), 2850 (4), 2875 (4), 2916 (4), 2937 (4), 2972 (6), 3010 (8), 3078 (3).

HCl Rupture from the Chloride. 13.5 g of chloride was gradually added from a dropping funnel to 7 g of KOH in 60 ml of the monoethyl ester of ethylene glycol which was heated to boiling. The hydrocarbon which formed was passed without condensation through a reflux condenser in which hot water circulated. The vapors were then condensed in a coil and collected in a receiver. Yield of hydrocarbon was 6.5 g (70%). Upon distillation, the hydrocarbon went over at 76.5-77°; n_D^{20} 1.4518. Upon prolonged storage the hydrocarbon polymerized completely.

Combined dispersion spectrum of the hydrocarbon:

254 (0.5), 361 (7), 437 (7), 523 (6), 811 (5), 860 (0.5), 899 (6), 1067 (1), 1144 (7), 1215 (10), 1290 (6), 1332 (6), 1380 (5), 1420 (0.5), 1453 (7), 1546 (0.5), 1559 (0.5), 1600 (9), 1623 (0.5), 1655 (15w).

The hydrocarbon reacted readily with maleic anhydride to form the polymer product, which is in agreement with the literature data [12].

0.6091 g of hydrocarbon was hydrogenated in the presence of platinum catalyst in alcoholic solution. Hydrogen used was 344 ml (0°, 760 mm), which corresponded to an excess of 3.4%, as against that calculated for the double bonds.

Hydrocarbon from the 54-78° Fraction. The hydrocarbon was distilled three times over metallic sodium. A hydrocarbon of b.p. 70-72° was isolated.

d_4^{20} 0.7514; n_D^{20} 1.4260; MR_D 27.96. $C_6H_{10}\,\lceil$. Calculated: MR_D 27.95 (the increment for a three-membered ring was adopted as equal to 0.7).

Combined dispersion spectrum:

229 (0.5), 265 (5 w), 392 (2), 412 (4), 475 (8), 482 (0.5), 530 (2), 696 (0.5), 713 (6), 729 (2), 818 (3), 895 (8 w), 968 (6), 992 (2), 1021 (3), 1094 (2 w), 1142 (1), 1191 (10), 1238 (1w), 1291 (2 i), 1331 (0.5), 1390 (5w), 1428 (5), 1458 (5), 1637 (10), 1648 (8), 2916 (3), 2989 (1), 3011 (8), 3081 (4w).

For determination of conjugated diene, the hydrocarbon was sealed in an ampoule with a titrated solution of maleic anhydride; the mixture was heated 4 hours on a boiling water bath. Unreacted maleic anhydride was extracted with hot water and titrated with alkali. The difference between maleic anhydride in the initial solution and in the solution after heating with the hydrocarbon made it possible to calculate the content of conjugated diene, which was found to be equal to 3%.

0.3830 g of hydrocarbon was hydrogenated in the presence of platinum catalyst in alcoholic solution. 110 ml of hydrogen was used for the hydrogenation (0°, 760 mm) which corresponded to an excess of 5%, calculating on one double bond basis.

II. Reaction of PBr_3 with Dimethylcyclopropylcarbinol

20 g of carbinol was added to 60 g of PBr_3 under the conditions described above for synthesis of the chloride. Yield of bromide was 86% of theory. Upon fractionation, almost no hydrogen was obtained. The bromide, which was dried over calcium chloride, boiled at 154-155°; d_4^{20} 1.2506; n_D^{20} 1.4780; MR_D 36.84. $C_6H_{11}Br$. Calculated: MR_D 37.18.

Analysis for bromine content gave somewhat high results.

Combined dispersion spectrum for bromide:

214 (6), 263 (1), 299 (0.5), 457 (3), 510 (0.5), 563 (8), 643 (10), 744 (2), 795 (2), 836 (1), 1205 (2), 1271 (2), 1313 (2), 1349 (2), 1382 (6), 1441 (5), 1618 (1), 1645 (1), 1672 (10), 2862 (3), 2914 (6), 2967 (4).

HBr Rupture from Bromide. Rupture was carried out under conditions described above for the chloride. 20 g of the bromide and 7.5 g of KOH as a solution in 80 ml of the monoethyl ester of ethylene glycol were taken. The resulting hydrocarbon boiled at 76-77°; n_D^{20} 1.4530. Upon prolonged storage the hydrocarbon polymerized completely.

The combined dispersion spectrum for the hydrocarbon was identical to the spectrum of the hydrocarbon which resulted from the chloride.

SUMMARY

1. By reaction of PCl_3 with dimethylcyclopropylcarbinol, there is formed up to 50% of an abnormal reaction product – 5-chloro-2-methylpentene-2. Formation of isopropenylcyclopropane is observed at the same time.

2. Upon reacting PBr_3 with dimethylcyclopropylcarbinol, only the abnormal reaction product – 5-bromo-2-methyl-pentene-2 – is formed.

3. The Bruylants and Favorskaya observations on conversion of 5-chloro-2-methyl-pentene-2 by saponification to dimethylcyclopropylcarbinol, have been spectroscopically confirmed. The data obtained also make it possible to assume that in addition to the above, there is also formed an unsaturated alcohol, of open carbon chain, upon saponification.

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* See Consultants Bureau Translation, page 243.

** See Consultants Bureau Translation, page 259.

*** See Consultants Bureau Translation, page 613.

**** See Consultants Bureau Translation, page 2225.

THE CONVERSION MECHANISM OF TERTIARY ALCOHOLS OF THE CYCLOPROPANE SERIES UNDER THE INFLUENCE OF MINERAL AND ORGANIC ACIDS

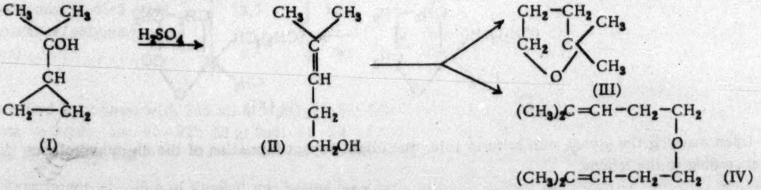
III. THE INTERACTION OF DIMETHYLCYCLOPROPYLCARBINOL, METHYLETHYLCYCLOPROPYLCARBINOL AND METHYLISOPROPYLCYCLOPROPYLCARBINOL WITH SULFURIC ACID

T. A. Favorskaya, N. V. Shcherbinskaya and E. S. Golovacheva

All of the known literature investigations on interaction of tertiary alcohols of the cyclopropane series with sulfuric acid have been carried out for the purpose of synthesizing and studying various hydrocarbons. To such belong those of Keersblick [1], Volkenburgh [2] and Slabey [3]; all of these authors used concentrated sulfuric acid, and therefore no other products were obtained than the dehydration products. In studying the interaction of dilute sulfuric acid with methylphenyl- and diphenylallyl-carbinols, the authors, with Sh. A. Fridman [4], established that these alcohols are ruptured, with simultaneous formation of acetophenone and benzophenone. Upon reacting methylphenylcyclopropylcarbinol with dilute sulfuric acid, there was observed, in addition to the formation of unsaturated hydrocarbon, and enlargement of the three-membered cycle into a four-membered, with formation of methylphenylcyclobutanol [5]. On the other hand, upon heating dimethyl- and methylethylcyclopropylcarbinols with dilute formic acid [6, 7], the authors succeeded in synthesizing a whole series of products, and in determining that the first substances formed during the reaction are the unsaturated primary alcohols of 2-methy-penten -2-ol-5 (II) and 3-methylhexen -3-ol-6 (VII), which then become cyclized into derivatives of tetrahydrofuran, and convert into a series of other compounds as well.

Because of a desire to determine by which of the above-described mechanisms interaction of aliphatic alcohols of the cyclopropane series takes place with sulfuric acid, the authors carried this reaction out with acid of varying concentration (1:4, 1:5 and 1:10).

With dimethylcyclopropylcarbinol (I), the first reaction product in all experiments carried out was found to be the primary alcohol (II), which then, on the one hand, isomerized into 2,2-dimethyltetrahydrofuran (III), and on the other – to form a small amount of ether (IV):

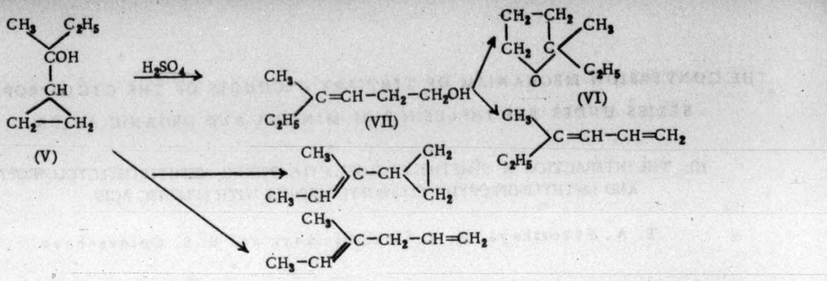


Dehydration of alcohol (I) to form the cyclic hydrocarbon, as used with concentrated sulfuric acid in the authors' experiments, was not observed. It was demonstrated that the concentration of acid affects considerably the yields of various reaction products: the lower the acid concentration the higher the yield of products (II) and (III) and the less of ester (IV) as well as resinous polymerization products.

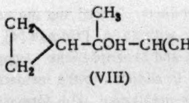
Reaction of Methylethylcyclopropylcarbinol (V). This was carried out only with sulfuric acid at a dilution of 1:5, since it was possible at this concentration to obtain all of the reaction products The authors isolated in this case a mixture of hydrocarbons which, according to the constants, corresponded to that resulting from the reaction of methylethylcyclopropylcarbinol [7] and formc acid; 2,2-methylethyltetrahydrofuran (VI), a primary alcohol – 3-methylhexen -3-ol-6 (VII), and a number of polymeric products. (See diagram at top of next page).

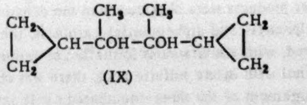
It was not possible in this instance to isolate a simple ether corresponding to alcohol (V).

The next alcohol investigated was methylisopropylcyclopropylcarbinol, prepared by reacting magnesium



isopropylbromide with acetyltrimethylene. There were obtained as the result of this reaction, in addition to alcohol (VIII), the glycol-2,3-dicyclopropylbutandiol-2,3 (XI).

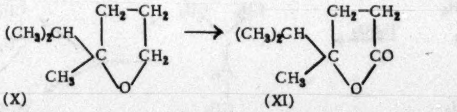

(VIII)


(IX)

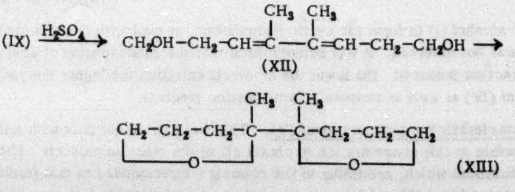
Slabey [3], who obtained methylisopropylcyclopropylcarbinol by the same procedure on a very small scale makes no reference to formation of this glycol. A small amount of this glycol was obtained by one of us [8]; however, it was not possible to carry out a more detailed investigation. The glycol was oxidized with lead tetraacetate according to the method of Criege [9], from which there resulted a single reaction product – acetyltrimethylene.

Both the alcohol and the glycol were reacted with dilute sulfuric acid (1: 10). In the case of the alcohol, the authors obtained 2,2-methylisopropyltetrahydrofuran; it was not possible to isolate the corresponding primary alcohol because of the small volume of alcohol (VIII) at the authors' disposal. Nevertheless, the authors consider it allowable in this case again to accept the same reaction mechanism as was applied to the first two alcohols investigated [6, 7].

The structure for 2,2-methylisopropyltetrahydrofuran (X), was proved by its oxidation with $KMnO_4$ solution, whereby the lactone of γ δ,dimethyl-γ-hydroxy-caproic acid (XI) resulted:

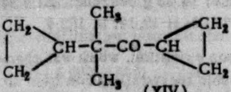


Upon reacting the glycol with sulfuric acid, one might expect formation of the ditetrahydrofuran derivative (XIII), according to the scheme:



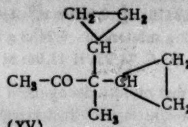
On the other hand, however, since glycol (IX) is a pinacol, then one might expect a pinacolic rearrangement, with formation of two possible pinacolines (XIV) and (XV): (See top of next page).

Experiments demonstrated that the reaction proceeds along both possible directions. A small amount of ketone was isolated from the reaction products, the composition of which corresponded to the formula $C_{10}H_{16}O$.



(XIV)

or



(XV)

The amount did not permit the authors to determine which of the two ketones resulted at the time. The main direction was apparently conversion of glycol into the unsaturated diprimary glycol (XII), but the presence of a conjugated double bond system in it caused immediate polymerization of the substance when a certain specific temperature was reached. The amount of glycol distilled was so small that it was possible only to determine the refractive index and the number of active hydrogen atoms, and to ascertain the presence of double bonds on the basis of rapid decolorization of $KMnO_4$ solution. All of these data indicated that, in all probability, reaction of pinacol with sulfuric acid was halted at the first stage of 1,3-diene glycol formation; however, cyclization of the latter to tetrahydrfuran did not occur.

EXPERIMENTAL

Dimethylcyclopropylcarbinol (I)

N. V. Shcherbinskaya

The carbinol was prepared from methyl magnesium bromide and acetyltrimethylene. The resulting crude alcohol was purified by oxidation ($KMnO_4$ solution). The yield of alcohol with b.p. 120 - 123° was 54 - 55% of theory.

Interaction of Dimethylcyclopropylcarbinol With Sulfuric Acid

In the three experiments carried out, acid of various concentrations was used, and at the same time the interaction period was decreased. Experiments carried out can be summarized in the following Table:

Reaction product	H_2SO_4(1: 4) 2 hours	H_2SO_4(1: 5) 2 hours	H_2SO_4(1: 10) 1 hour
	(in %)	(in %)	(in %)
Dimethyltetrahydrofuran	31.1	44.1	51.6
2-Methylpenten -2-ol-5	—	1	5.0
2-Methylpenten-2-ol-5 ether. . . .	13.5	10.0	—
Resinous residue (polymerization product)	8.0	7.5	Small amount

Experiment I. 30 g of alcohol was boiled for 2.5 hours with 125 ml of H_2SO_4 (1: 4). The reaction products were extracted with ether and washed with soda solution. The following fractions resulted upon distillation. 1st: 90 - 92°, 9.4 g; 2nd: 103 - 105° at 13 mm, 3.7 g and the resinous residue was 2 g.

Experiment II. 68 g of alcohol was boiled for 2 hours with 240 ml of H_2SO_4 (1: 5). After similar treatment and distillation, the following fractions were isolated: 1st: 90 - 92°, 30 g; 2nd: 61 - 63° at 11 mm, 0.65 g; 3rd: 101 - 103° at 10 mm, 6.2 g; 4th: weight of resin was 4.2 g.

Experiment III. 40 g of alcohol was boiled for 1 hour with 220 ml of H_2SO_4(1: 10). The following fractions were obtained after similar treatment: 1st: 90 - 92°, 20.65 g, 2nd: 61 - 63° at 11 mm, 2.0 g. There remained in the flask only a very negligible amount of resin.

Furthermore, in all three experiments there resulted fractions with b.p. 92 - 110° — a mixture of tetrahydrofuran and acetyltrimethylene — which gave a 2,4-dinitrophenylhydrazone precipitate with m.p. 145 - 146°. The pure acetyltrimethylene was not isolated from these fractions because of its small volume. As was indicated above [6], the acetyltrimethylene is usually present in small amount with the dimethylcyclopropylcarbinol.

The fraction with b.p. 61 - 63° at 11 mm corresponded to the primary alcohol (II):

d_4^{20} 0.8573; n_D^{20} 1.4460; MR_D 30.74. $C_6H_{12}O$. Calculated: MR_D 31.20.
0.1332 g substance: 31 ml CH_4 (21°, 756.8 mm).

The fraction with b.p. 101 - 103° at 10 mm (115 - 116° at 25 mm) gave negative test for hydroxyl and carbonyl groups: on the basis of the analytical data for this fraction, the formula which should be attributed to it is that of a simple ether (VI).

d_4^{20} 0.8416; d_4^{0} 0.8570; n_D^{20} 1.4530; MR_D 58.06. $C_{12}H_{22}O_2$. Calculated: MR_D 58.32.
0.1192 g substance: 0.3452 g CO_2; 0.1272 g H_2O. 0.1213 g substance; 14.23 g benzene: Δt 0.24°.
Found %: C 78.97; H 11.94; M 182.2. $C_{12}H_{22}O$. Calculated %: C 79.05; H 12.16; M 182.0.

The ether rapidly decolorized $KMnO_4$ solution, and gave acetone upon oxidation, which was characterized through its 2,4-dinitrophenylhydrazone, with an m.p. of 125 - 126°, after double recrystallization from alcohol. A mixed sample did not give depression. It was not possible to isolate any other oxidation products. The resinous residue in the distilling flask was evidently the hydrocarbon polymerization product, which can be formed by dehydration of the primary alcohol (II).

Methylethylcyclopropylcarbinol (V)

The alcohol was prepared from ethyl magnesium bromide and acetyltrimethylene. The resulting product, with b.p. 138 - 144°, was purified by oxidation with $KMnO_4$ solution to remove unsaturated additives. The yield of pure alcohol, with b.p. 141 - 143°, was 54% of theory.

Interaction of Methylethylcyclopropylcarbinol With Sulfuric Acid

50 g of methylethylcyclopropylcarbinol was boiled for 2 hours with 120 ml of H_2SO_4 (1: 5). The reaction products were extracted with ether, the extracts washed with soda solution. After drying and distilling off the solvent, the products were distilled at first under atmospheric pressure. The following fractions resulted from repeated fractionations: 1st 100 - 107°, 12.5 g (29%), 2nd 107 - 112°, 2g (~5.5%), 3rd 119 - 121°, 12.0 g (24%). The residue was fractionated in vacuo, whereupon there resulted 0.5 g of substance with b.p. 69 - 71° at 11 mm. There also remained in the flask 1.5 g of resin.

The fraction with b.p. 100 - 107° was a mixture of hydrocarbons. Its purification from traces of acetyltrimethylene was carried out by means of heating with metallic Na. A substance resulted with boiling point 100 - 106°, d_4^{20} 0.7852, n_D^{20} 1.4425. The constants obtained were very close to the constants for the hydrocarbon mixture isolated from reaction products of methylethylcyclopropylcarbinol with formic acid [7].

The fraction with b.p. 107 - 112° was found to be acetyltrimethylene; from it resulted the 2,4-dinitrophenylhydrazone with m.p. 145° (from alcohol).

The fraction with b.p. 119 - 121°, n_D^{20} 1.4228, was found to be 2,2-methylethyltetrahydrofuran

The substance with b.p. 69 - 71° at 11 mm, n_D^{20} 1.4500, corresponded to the primary alcohol — 3-methylhexen -3-ol-6.

0.0998 g substance: 21 ml CH_4 (15°, 758.5 mm). Yield OH No. 0.997. $C_7H_{14}O$. Calculated OH No. 1.

Methylisopropylcyclopropylcarbinol (VIII)

E. S. Golovacheva

62 g (0.5 mole) of isopropyl bromide was added to 12 g of magnesium covered with ether. After termination of the addition, the reaction mixture was stirred for 2 hours, after which the acetyltrimethylene was added in an equal volume of ether in the amount of 32 g (3/4 of the theoretical amount, since a portion of the magnesium did not enter into reaction). The reaction mixture was further stirred and heated for 1 hour and left overnight. The reaction products, after decomposition of the organo-magnesium complex with water and dilute H_2SO_4, were extracted with ether and the extract washed with soda solution and dried with potash. After distilling off the ether, and distilling at 3 mm, 2 substances were isolated: 1) with a b.p. of 45 - 46°, 13 g (26.6%), and 2) with a b.p. of 128 - 130°, 2 g (6.17%). The second substance crystallized in the receiver.

Investigation of the substance with b.p. 45 - 46° at 3 mm. It boiled at 61.5 - 62° at 17 mm, 75 - 78° at 38 mm.

n_D^{20} 1.4465; d_4^{20} 0.8888; MR_D 38.47; $C_8H_{16}O$. Calculated MR_D 39.13. Slabey data for methylisopropylcyclopropylcarbinol [3].

n_D^{20} 1.4465; d_4^{20} 0.8856; MR_D 38.63.
0.0752 g substance: 0.2063 g CO_2; 0.0840 g H_2O. 0.1016 g substance: 19.8 ml CH_4 (13°, 752.8 mm).
Found %: C 74.85; H 12.49; number of active hydrogens 0.99. $C_8H_{16}O$. Calculated %: C 75.00; H 12.50; number of active hydrogens 1.0.

Investigation of the substance with b.p. 128 - 130° at 3 mm. The crystals pressed out on a porous plate melted at 71 - 72°.

Recrystallization from alcohol did not increase the melting point.

0.0911 g substance: 0.2359 g CO_2; 0.0865 g H_2O; 0.1198 g substance; 11.1 g benzene: Δt 0.256°. Found %: C 70.62; H 10.60; M 213. $C_{10}H_{18}O_2$. Calculated %: C 70.59. H 10.59; M 170.

Oxidation of the Glycol with Lead Tetraacetate. 1 g of the glycol and 5 g of freshly-prepared lead tetraacetate (an excess) were heated on a water bath at 50 - 60° for 2 hours. After cooling, the flask contents were neutralized with soda, the precipitated salts filtered off, the filtrate distilled, and the resulting product treated with a solution of 2,4-dinitrophenylhydrazine. The 2,4-dinitrophenylhydrazone which precipitated, and which gave an m.p. of 145°, did not give depression when mixed with the 2,4-dinitrophenylhydrazone of acetyltrimethylene.

Reaction of Sulfuric Acid With Methylisopropylcyclopropylcarbinol (VIII)

10 g of the alcohol in 110 ml of sulfuric acid (1: 10) was heated to boiling, with vigorous stirring, for 1 hour. The reaction products were extracted with ether and washed with soda solution, followed by drying with potash. After removing the ether by distillation, the residue was twice distilled over metallic sodium to remove acetyltrimethylene impurity, small amounts of which were found to be present in the initial alcohol. A substance with b.p. 141 - 143° resulted, possessing a pleasant aroma.

n_D^{20} 1.4310; d_4^{20} 0.8624; MR_D 38.40. $C_8H_{16}O$. Calculated: MR_D 38.59.
Literature data for 2,2-methylisopropyltetrahydrofuran [10]: b.p. 142 - 143°; d_4^{21} 0.8690; n_D^{21} 1.4285; MR_D 37.93.

0.0990 g substance: 0.2714 g CO_2; 0.1115 g H_2O. Found %: C 74.82; H 12.60. $C_8H_{16}O$. Calculated %: C 75.00; H 12.50.

The substance did not contain a hydroxyl group, was slowly oxidized by $KMnO_4$ solution (oxidation lasted for 48 hours). Neutral products did not result. The acid oxidation products were extracted with ether and dried with Na_2SO_4. After distilling off the ether, followed by distillation of the product, a substance with b.p. 97° at 8 mm (0.6 g) was isolated.

n_D^{20} 1.4500; d_4^{20} 0.9970; MR_D 38.29. $C_8H_{14}O$. Calculated: MR_D 38.60.
0.1083 g substance: 10 ml NaOH (T 0.003764): 1.5 ml HCl (T 0.003492).

0.1182 g substance: 0.0480 g Ag. Found: neut. equiv. 135.8; %: Ag 40.61. $C_8H_{14}O_2$. Calculated neut. equiv: 142; $C_8H_{15}O_3Ag$. Calculated %: Ag 40.45.

To determine neutralization equivalent, the substance was heated with 10 ml of alkali to complete dissolution, and the alkali excess titrated with hydrochloric acid. To obtain the silver salt, the lactone was dissolved in ammonia with heat, on a water bath, and ammonia excess removed by evaporation. Concentrated $AgNO_3$ was added to the resulting solution of ammoniacal salt of γ, δ-dimethyl-γ-hydroxycaproic acid. The precipitated silver salt was filtered off, washed with water and alcohol, and dried in a vacuum desiccator. Thus was obtained, as a result of oxidation of the substances with b.p. 141 - 143°, the lactone-γ, δ-dimethyl-γ-hydroxycaproic acid. Thus, there resulted on interaction of methylisopropylcyclopropylcarbinol with sulfuric acid, 2,2-methylisopropyltetrahydrofuran

Reaction of Sulfuric Acid With Glycol (IX)

10 g of 2,3-dicyclopropylbutandiol-2,3 was heated to boiling, with constant stirring, with 100 ml of dilute sulfuric acid (1: 10) for 1 hour. The liquid became very dark. After extraction of the reaction products with ether, following this by drying and removal of the solvent by distillation, there remained a dark, viscous oil, which resinified when attempt was made to distill it at 17 mm.

A second experiment was carried out with more dilute sulfuric acid (1: 15). The resulting light oil resinified upon distillation at 5 mm. A third experiment was carried out with the acid (1: 10) in a CO_2 atmosphere. Ether extractions of the reaction products were washed with soda solution and dried with Na_2SO_4. After distilling off the ether, the residue was distilled at 5 mm in a stream of CO_2. The following fractions resulted: 1st, 18 - 25°, 0.5 g; 2nd, 25°, 0.6g; the temperature then rose rapidly to 75°, and 1 g of distillate was collected; at 75°, all of the material remaining in the distilling flask immediately polymerized.

The fraction with b.p. 25° at 5 mm did not contain hydroxyl, did not decolorize $KMnO_4$ solution, and did give a 2,4-dinitrophenylhydrazone, with m.p. 181.5 - 182° (from alcohol).

n_D^{20} 1.4300; d_4^{20} 0.8678; MR_D 45.27; $C_{10}H_{16}O$. Calculated: MR_D 45.21.

0.0943 g substance: 0.2786 g CO_2; 0.0912 g H_2O. 0,1059 g substance; 12.41 g benzene: Δt 0.284°.

Found %: C 78.86; H 10.86; M 154.6. $C_{10}H_{16}O$. Calculated %: C 78.96; H 10.53; M 152.

Analysis of the 2,4-dinitrophenylhydrazone:

0.0962 g substance: 15.8 ml N_2 (17°; 767 mm). Found %: N 16.41. $C_{16}H_{21}O_4N_4$. Calculated %: N 16.81.

The substance boiling at 75°, 5 mm, was in the form of a mobile liquid of yellow color.

n_D^{20} 1.4790. 0.0317 g substance: 7.5 ml CH_4 (15.5°, 769 mm). Found: number of active hydrogens 2. $C_{10}H_{18}O_2$. Calculated: number of active hydrogens 2.

It was, in all probability, the unsaturated di-primary glycol (XII).

SUMMARY

1. The interaction of dimethylcyclopropyl-, methylethylcyclopropyl- and methylisopropylcyclopropylcarbinols with sulfuric acid has been studied.

2. It has been established that the first alcohol forms 2-methylpentene-3-ol-5, which then converts into 2,2-dimethyltetrahydrofuran and into the ester; the second alcohol gives 3-methylhexen-3-ol-6, 2,2-methylethyltetrahydrofuran and a mixture of unsaturated hydrocarbons; the third alcohol converts into 2,2-methylisopropyltetrahydrofuran.

3. It has been demonstrated that in the organomagnesium synthesis of methylisopropylcyclopropylcarbinol, there results the tertiary alcohol, 2,3-dicyclopropylbutandiol-2,3 which, when reacted with dilute sulfuric acid, converts into one of several possible ketones.

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* See Consultants Bureau Translation, page 437.

** See Consultants Bureau Translation, page 1553.

*** See Consultants Bureau Translation, page 1731.

INVESTIGATION IN THE FIELD OF COMPOUNDS CONTAINING THREE-MEMBERED OXIDE RINGS

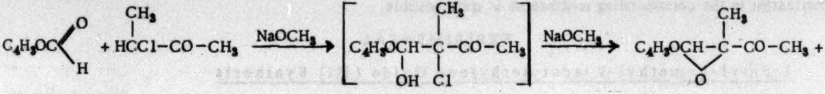
IX. CONDENSATION OF α-HALOKETONES WITH FURFURAL

V. F. Martynov

Several years ago the authors developed a new synthetic procedure for aliphato-aromatic α-ketoxides, produced by the condensation of aliphatic α-haloketones with benzaldehyde in the presence of sodium methylate [1]. The author has carried out condensation of benzaldehyde with chloroacetone, chloromethylketone and α-chloroethylmethylketone. The corresponding products resulted in good yields for all cases. This reaction was extended to other aliphatic α-haloketones [2].

The present work has for its purpose an extension of this reaction to the field of heterocyclic aldehydes, of which, at present, only furfural has so far been used. The author carried out condensation of α-haloketones with furfural as in the case of benzaldehyde, and in the presence of sodium methylate.

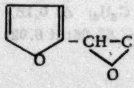
The mechanism for a similar type of condensation reaction can be illustrated by the Claisen condensation scheme [3].



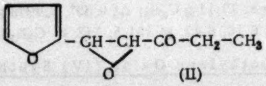
$$C_4H_3OCHO + HCCl(CH_3){-}CO{-}CH_3 \xrightarrow{NaOCH_3} \left[C_4H_3OCH(OH){-}C(CH_3)(Cl){-}CO{-}CH_3\right] \xrightarrow{NaOCH_3} C_4H_3OCH{-}C(CH_3){-}CO{-}CH_3 +$$

$+NaCl + CH_3OH.$

Condensation of furfural was carried out with chloroacetone, chloromethylethylketone, α-chloroethylmethylketone and chloroacetophenone. In all cases, reaction proceeded in a manner similar to that for benzaldehyde; however, not all of the condensation products were trapped. Thus, the condensation product of furfural with chloroacetone, which should have been furfuralacetone oxide (1-furyl-2-acetyl-oxide-ethane) (I) could not be isolated, despite several reruns of this reaction. Instead of an individual product, a resinous mass was obtained, which did not undergo fractionation. The same picture was observed when condensation of furfural with α-chloromethylethylketone was carried out The author did not succeed in obtaining 1-furyl-2-propionylethylene oxide (II):



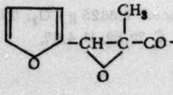
(I)



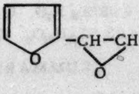
(II)

Instead of the expected compound, the author obtained a resinous mass. It should be mentioned that both reactions by external appearance apparently proceed normally, i.e., heat evolution and separation of a copious sodium precipitate were observed.

Only when condensing furfural with α-chloroethylmethylketone, did the author finally succeed in synthesizing an individual product – 1-furyl-2-methyl-2-acetyl-ethylene oxide (III). It should be mentioned that in the formation of this stable keto-oxide there was no such intense darkening of the reaction mixture as was the case in the preceding instances.



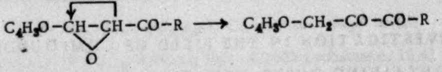
(III)



(IV)

On the grounds of the data, it might be assumed that the corresponding keto oxides were formed in the case of furfural with chloroacetone and α-chloromethylethylketone condensation, and that they could have resinified, however, in the presence of the alkaline reagent, sodium methylate.

This resinification can be represented as follows, via the preliminary formation from keto oxide of the α-diketone.



$C_4H_3O-CH_2-CO-CO-R$

Similar isomerizations are known from the literature for aliphato-aromatic α-keto oxides, proceeding under the influence of various reagents, among them alkaline [4]. The resulting α-diketones, judging for example from 1-phenylbutandione-2,3, are quite unstable [5].

It might be expected, therefore, that this instability would be increased many-fold upon passing to diketones of the furfural series. If this point of view is taken, there can then be clarified as well the relatively high stability of 1-furyl-2-methyl-2-acetylethylene oxide. Formation of the α-diketone in such case would be difficult, since it is connected with replacement of a methyl group and not of a hydrogen.

1-Furyl-2-methyl-2-acetylethylene oxide (III) is a substance which is thermally quite stable; it distills readily in vacuo without noticeable resinification; all attempts to obtain the semicarbazone, however, failed; the crystalline derivative did not precipitate, and there was only observed a strong darkening of the reaction mixture. However, analyses, molecular weight, refraction and analogy in formation to the corresponding keto oxide of the benzaldehyde series [1] does not leave any doubts as to the structure of this compound.

Upon condensing furfural with chloroacetophenone, the author obtained furylbenzoyl-ethylene oxide (IV). Crystalline, colorless compound, changing readily in the air; after 2 - 3 days the crystals darkened and converted to a liquid. In the light of the above-presented concept, such a ready change becomes clear, since in this case isomerization to the corresponding α-diketone is quite possible.

EXPERIMENTAL

1-Furyl-2-methyl-2-acetylethylene Oxide (III) Synthesis

Freshly-distilled furfural and α-chloroethylmethylketone were used to carry out the reaction. 50 g of α-chloroethylmethylketone and 60 g of furfural were diluted with 50 ml of methyl alcohol. A solution of 10 g of sodium in 150 ml of methyl alcohol was added dropwise, with vigorous stirring, to the mixture cooled in ice water. After treatment of the reaction mixture with water, the oil which separated was extracted with ether. The ether extract was dried with sodium sulfate. After distilling off the ether, the residue was fractionated twice in vacuo. 32 g of greenish-yellow liquid with b.p. 72 - 73° at 1 mm resulted. The yield was 41% of theory.

d_4^{16} 1.1384; n_α^{16} 1.49159; MR_α 42.27. $C_9H_{10}O_3$. Calculated MR_D 42.18.

0.1754 g substance: 0.4190 g CO_2; 0.0963 g H_2O. 0.1525 g substance: 0.3646 g CO_2; 0.0840 g H_2O. 0.2136 g substance; 17.11 g C_6H_6; Δt 0.39°. 0.0976 g substance; 17.11 g C_6H_6: Δt 0.18°. Found %: C 65.15, 65.2; H 6.10, 6.12; M 161.5, 158.1. $C_9H_{10}O_3$. Calculated %: C 65.06; H 6.02; M 166.

Furylbenzoylethylene Oxide (IV) Synthesis

10 g of chloroacetophenone was diluted with 15 ml of methyl alcohol, and 11 g of furfural then added. A solution of 1.5 g of sodium in 30 ml of methyl alcohol was added dropwise, with stirring, to the mixture cooled in ice water. No resinification was observed during the reaction; after completion of the condensation, a light-yellow liquid was formed, of weak alkaline reaction. A light precipitate of sodium chloride settled down to the bottom of the flask. The reaction mixture was treated with water, weakly acidified with acetic acid, and an ether extraction then made, which was dried with sodium sulfate. After distilling off the ether, the residue crystallized. The crystals isolated weighed 6 g (40%). For purification they were first crystallized from methyl alcohol and then from petroleum ether. Almost colorless crystals resulted with m.p. 58 - 59°.

0.0888 g substance: 0.2372 g CO_2; 0.0372 g H_2O. 0.1352 g substance: 0.3625 g CO_2; 0.0560 g H_2O. Found %: C 73.06, 73.12; H 4.67, 4.63. $C_{13}H_{10}O_3$. Calculated %: C 72.89; H 4.67.

SUMMARY

1. The condensation of furfural with chloroacetone, chloromethylethylketone, α-chloroethylmethylketone and chloroacetophenone in the presence of sodium methylate has been investigated.

2. The oxides of 1-furyl-2-methyl-2-acetylethylene and 1-furyl-2-benzoylethylene, unknown in the literature, have been synthesized and characterized.

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A STUDY OF HYDROXYDIHYDROFURANS

III. INTERACTION OF 2,4,5-TRIPHENYL-5-METHYL-2-HYDROXYDIHYDROFURAN 2,5 WITH ACETIC ANHYDRIDE

E. D. Venus-Danilova and A. N. Orlova

In the preceding article [1], the authors described properties for the interaction product between 2,4-diphenyl-5,5-dimethyl-2-hydroxyfuran -2,5 and acetic anhydride, and it was established that this substance is phenyl-(1-phenyl)-isocrotylacetoacetic acid.

Of interest was the question as to whether other substituted hydroxyhydrofurans are capable of similar reaction or not, and the problem of how stable the substituted acetoacetic acids formed during this reaction are with respect to the nature of radicals in the 5- position of the original hydroxydihydrofuran For solution of this problem, the authors selected 2,4,5-triphenyl-5-methyl-2-hydroxydihydrofuran -2,5 (I), which differs from the earlier-investigated hydroxydihydrofuran in the fact that one methyl radical in position 5 is replaced by the phenyl radical.

2,4,5-Triphenyl-5-methyl-2-hydroxydihydrofurane-2,5 was isolated, among other products, by reaction of 40% sulfuric acid with symmetrical methyldiphenylphenyl acetylenylethylene glycol (2,3,5-triphenylpentyne-4-diol-2,3) [2]. By interacting this hydroxydihydrofuran with acetic anhydride under conditions described in the preceding article [1], a crystalline substance of the empirical formula $C_{25}H_{22}O_3$ was obtained.

The substance possessed unsaturation (decolorization of aqueous potassium permanganate and bromine in chloroform), and acid properties – soluble in dilute aqueous alkalie and carbonate solutions, and precipitated again by neutralization of the solutions Titration with alkali and determination of the number of active hydrogens indicated that the substance contained only one carboxyl group.

In contrast to the acid product described previously, which resulted from interaction of 2,4-diphenyl-5,5-dimethyl-2-hydroxydihydrofuran -2,5 with acetic anhydride, the ammoniacal salt of this compound did not precipitate upon passage of gaseous ammonia into an ether solution of the product.

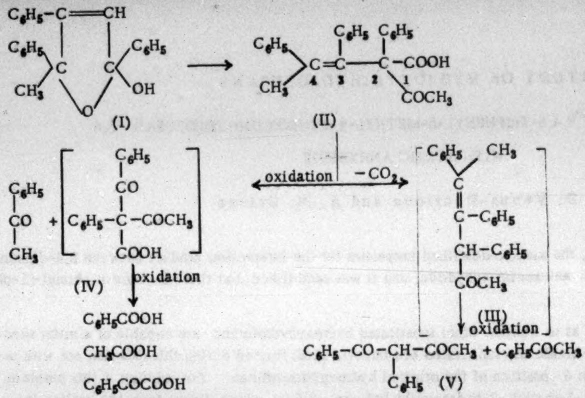
According to the standard reactions, no carbonyl group was found in the compound, to which the authors, by analogy with the acid previously obtained [1], attributed the structure of an unsaturated, substituted β-keto acid (II). A similar phenomenon was also observed previously for phenyl-(1-phenyl)-isocrotylacetoacetic acid.

The substance was oxidized with potassium permanganate in aqueous, weakly alkaline medium. Oxidation took place much more readily than for the analogous acid described earlier [1]. Upon oxidation in neutral medium, only carbon dioxide, acetophenone and the β-diketone – phenylacetylbenzoylmethane (1,2-diphenylbutandione-1,3) – were isolated; in alkaline medium, acetophenone, a smaller amount of the β-diketone, and very small amounts of formic, acetic, benzoic and benzoylformic acids were isolated. It is possible that in neutral medium rapid decarboxylation of the original acid proceeds, with formation of the unsaturated ketone (III), which upon oxidation, yields only neutral products. In alkaline medium, decarboxylation is slowed down, and therefore formation of acids (scheme) is also possible, along with neutral substances.

The fact that traces of formic acid were obtained can be explained by oxidation of the enolic form of β-diketone. (See top of next page).

However, the diketo acid (IV) and the unsaturated ketone (III) were not found among the oxidation products. On the other hand decarboxylation of the unsaturated β-keto acid (II) by boiling with water, or by heating in the dry state, was confirmed by carbon dioxide evolution.

Properties of the compound synthesized by the authors indicated that this substituted acetoacetic acid – 2,3,4-triphenyl-2-acetylpenten-3-acid (II) – was a considerably less stable compound than phenyl-(1-phenyl)-isocrotylacetoacetic acid, which evidently depends upon the presence of phenyl at carbon atom number 4 in the unsaturated acid molecule (II).



EXPERIMENTAL

The initial 2,4,5-triphenyl-5-methyl-2-hydroxydihydrofuran -2,5 (m.p. 125 - 126°) was prepared according to the previous directions by one of us with L. A. Pavlova [2], in 21.6% yield, calculating on the basis of original acetylene α-glycol.

I. Synthesis and properties of $C_{25}H_{22}O_3$ Acid.

Upon heating a mixture of hydroxydihydrofuran and acetic anhydride to boiling (135 - 140°), considerable resinification was observed; this reaction, therefore, was carried out at lower temperature.

A solution of 1 g of hydroxydihydrofuran and 6 g of acetic anhydride was heated for 45 minutes on an oil bath at a temperature of 120°. Upon cooling, the light-yellow reaction mass was poured into 20 - 30 times the volume of ice water, with vigorous stirring; on standing, small lumps precipitated by the following day, which were ground in a mortar with water, and washed repeatedly with water (to a negative reaction for acid). After drying in air, a faintly-yellow compound, m.p. 82 - 83° (with decomp.) resulted. Because of its instablity, the substance failed to crystallize.

Synthesis of the substance was repeated several times under identical conditions. 7.35 g of substance (86 %) was synthesized from 7.5 g of hydroxydihydrofuran, and after thorough washing with water, gave an m.p. of 82 - 83° (decomp.).

0.1114 g substance: 0.3298 g CO_2; 0.0608 g H_2O. 0.1001 g substance: 0.2965 g CO_2; 0.0541 g H_2O. Found %: C 80.74, 80.78; H 6.06, 6.00. $C_{25}H_{22}O_3$. Calculated %: C 81.08; H 5.95. 0.0837 g substance: 5.6 ml CH_4 (18°, 760 mm). Found: ν_0 5.25 ml; % OH 4.78. $C_{25}H_{21}O_2(OH)$. Calculated ν_0 5.07 ml; % OH 4.58.

0.0594 g substance: 1.9 ml 0.1 N NaOH (T 0.00400). No. of carboxyl groups found 1.2. $C_{25}H_{22}O_3$. No. of carboxyl groups calculated - 1.

The substance decolorized a solution of bromine in chloroform, and reacted with an aqueous solution of potassium permanganate. It did not react under standard conditions with semicarbazide, hydroxylamine or 2,4-dinitrophenylhydrazine

II. Oxidation of $C_{25}H_{22}O_3$ acid.

a) Oxidation in weakly alkaline medium. 2.5 g of the substance, 0.3 g of sodium hydroxide, and 2 g of potassium permanganate solution in 100 ml of water were heated to 40° with vigorous stirring. After about 0.5 hours, decolorization had occurred, following which another 2 g of oxidant ground to a powder was added in 3 portions (according to theoretical calculations, 3.6 g of potassium permanganate would be required for 1 mole of initial substance, on the basis of 5 active oxygen atoms). Oxidation was complete after 2 hours.

The neutral oxidation products were removed from the manganese dioxide precipitate and from the filtrate by ether. After removal of the ether, the oily precipitate began to crystallize partially. All of the substance was converted to the semicarbazone, which, after recrystallization, melted at 195 - 196.5°, corresponding to acetophenone semicarbazone (mixed sample test). The yield of acetophenone, recalculated from 1 g of the semicarbazone, amounted to 0.7 g (86.4%).

After isolation of the acetophenone, a stream of carbon dioxide was passed into the aqueous solution to tie up excess alkali and to decompose the diketone enolate, after which the neutral oxidation products volatile with steam were distilled into a solution of p-nitrophenylhydrazine. A yellow precipitate resulted immediately, with m.p. 136 - 137°, corresponding to the pyrazole obtained from the β-diketone – acetylbenzoylphenylmethane (mixed sample test) – described in Communication I.

No other products were found in the ether extract obtained from the residue after distilling the β-diketone.

Benzoylformic acid was found in a sample of the organic salt solution (the formation of a yellow interaction product with phenylhydrazine hydrochloride, with m.p. 153° [3]). After concentrating the salt solution on a water bath, and decomposing it with dilute sulfuric acid, a small amount of benzoic acid (about 0.07 g) was obtained by sublimation, which was characterized by its m.p. and by mixed sample. Traces of formic acid were found in the filtrate distillate (turbidity of mercuric chloride solution, blackening of silver nitrate).

A small amount of silver salts was obtained from the second and third fractions of the distillate, turning black upon heating, decomposed and removed by repeated boiling and filtration. The silver content – silver acetate – was determined in the residue (about 0.08 g). Found %: Ag 64.89. $C_2H_3O_2Ag$. Calculated %: Ag 64.65.

b) Oxidation in neutral medium. 2.5 g of the substance was oxidized with 100 ml of an aqueous solution of potassium permanganate (1.4 g theoretically required, calculating on the basis of 2 active oxygen atoms per mole of substance) at a temperature of 40°. Reaction time was 2 hours. The carbon dioxide evolved during reaction was trapped in a Tishchenko flask with baryta water. The ether extract of filtrate and precipitate was washed with 30 ml of 3% sodium hydroxide solution to separate the β-diketone. After evaporation of the ether, actophenone resulted, characterized as its semicarbazone, with m.p. 195 - 196°. 0.52 g of semicarbazone resulted, corresponding to a 70% yield of acetophenone.

After extraction of acetophenone, the alkaline solution was neutralized with dilute sulfuric acid, and acetylbenzoylphenylmethane volatile with steam was distilled out of the solution and extracted with ether. After distilling off the ether, 0.75 g of a paraffin-like mass was separated, which solidified into a substance with m.p. 90 - 92°, found from its properties to be identical with acetylbenzoylphenylmethane described in the preceding article [1]. Pyrazole obtained from it had an m.p. of 137 - 138°, corresponding to the pyrazole described in preceding experiments (mixed sample).

Upon acidification of a concentrated aqueous solution of organic acid salts, obtained after removal of the neutral oxidation products, 0.9 g of the initial compound was obtained. After its separation from the filtrate, no organic acids were found, except for traces of formic acid.

SUMMARY

1. By reaction of acetic anhydride with 2,4,5-triphenyl-5-methyl-2-hydroxydihydrofuran - 2,5, the β-keto acid $C_{25}H_{22}O_3$ – 2,3,4-triphenyl-2-acetylpenten-3 acid has been synthesized.

2. It has been established that this acid is considerably less stable than phenyl(1-phenyl)-isocrotylacetoacetic acid, described earlier.

3. An assumption has been made that a decrease in stability of the acid obtained depends upon the presence of a phenyl group in the 5-position of hydroxyhydrofuran.

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* See Consultants Bureau Translation, page 707.

** " " " " " a-197.

[illegible] were clarified [illegible] a solution of [illegible] m.p. 185-187°, corresponding to the [illegible] (mixed sample [illegible]) [illegible] in Comptes Rendus [illegible]

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1. By reaction of [illegible]

2. It has been established that [illegible] described earlier.

3. An assumption has been made that [illegible] of a phenyl group in the [illegible]

LITERATURE CITED

[1] [illegible]

[2] [illegible]

[3] A. E. [illegible]

Received December 31, 1952

[illegible] Institute of Technology
[illegible] Laboratory

[illegible] See Comptes Rendus [illegible], page 101.

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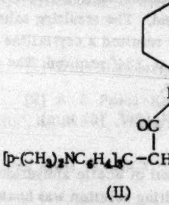
CONDENSATION PRODUCTS OF TRIPHENYLCARBINOLS WITH 1-PHENYL-3-METHYLPYRAZOLONE-5. II.

O. F. Ginzburg

It was demonstrated in the preceding article [1] that 4,4'-tetramethyldiaminotriphenylcarbinol enters readily into a condensation reaction with 1-phenyl-3-methylpyrazolone-5. This is explicable on the basis that 4,4'-tetramethyldiaminotriphenylcarbinol contains quite a mobile hydroxyl group; it might therefore be expected that 9-phenyl-9-hydroxy-10-methyl-9,10-dihydroacridine, in which the hydroxyl group is quite mobile, would, in its turn, enter readily into condensation with 1-phenyl-3-methylpyrazolone-5. Experiments carried out have confirmed this assumption: 1-phenyl-3-methyl-4-(9'-phenyl-10'-methyl-9',10'-dihydroacridyl-9')-pyrazolone-5 (I) was formed in almost 90% yield upon heating in methyl alcohol equimolecular amounts of 9-phenyl-9-hydroxy-10-methyl-9,10-dihydroacridine and 1-phenyl-3-methylpyrazolone-5. Compound (I) was an almost colorless, crystalline substance, and upon its dissolution in polar solvents, colored solutions were formed. Thus, for example, a solution of compound (I) in glacial acetic acid was colored yellow, in nitrobenzene it was colored orange. Coloration of the above-indicated solutions attests to the decomposition of compound (I) into ions resulting from rupture of the bond between the 9'-carbon atom of the acridine part of the molecule, and the 4-carbon atom of the pyrazolone ring.

Condensation of aminotriarylcarbinols, or of their methyl esters, with 1-phenyl-3-methylpyrazolone-5 also proceeds in benzene. Thus, for example, when a benzene solution containing equimolecular amounts of the methyl ester of 4,4',4''-hexamethyltriaminotriphenylcarbinol and 1-phenyl-3-methylpyrazolone-5 was heated, 1-phenyl-3-methyl-4-(p,p',p''-hexamethyltriaminotriphenylmethyl)-pyrazolone-5 (II) was formed, which was isolated from the benzene solution by dilution of the latter with gasoline.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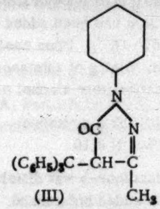
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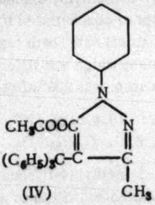
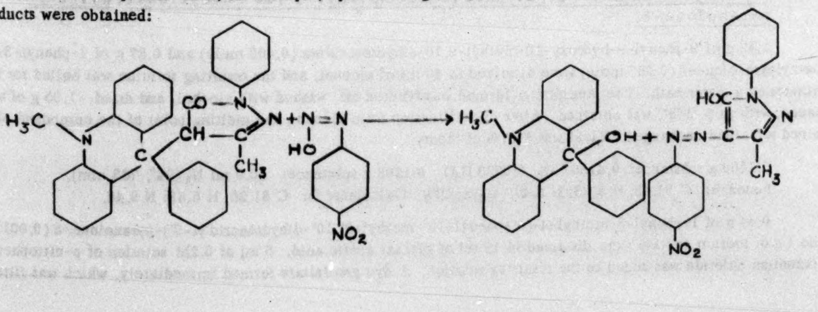

(IV)

Upon dissolution of (II) in glacial acetic acid, nitrobenzene, alcohol, and other polar solvents, violet-colored solutions resulted.

As with other compounds [2], which contain the 1-phenyl-3-methylpyrazolone-5 radical,(I) and (II) reacted with the diazo compound. Thus, for example, upon reacting compound (I) with p-nitrodiazobenzene, the following products were obtained:



This reaction also bears out the lability of the bond between the acridine and pyrazolone parts of the molecule.

It was mentioned in the preceding article that triphenylcarbinol in alcohol medium does not enter into condensation with 1-phenyl-3-methylpyrazolone-5. Further experiments indicated that under more rigorous conditions, namely in glacial acetic acid medium, triphenylcarbinol reacts with 1-phenyl-3-methylpyrazolone-5. In this case 1-phenyl-3-methyl-4-triphenylmethylpyrazolone-5 (III) is formed. Compound (III) acylated with acetic anhydride. Resulting from the acylation was 1-phenyl-3-methyl-4-triphenylmethyl-5-acetoxypyrazole (IV), which was also obtained by heating equimolecular amounts of triphenylcarbinol and 1-phenyl-3-methylpyrazolone-5 in acetic anhydride. As with compounds (I) and (II), compound (III) entered into reaction with diazo compounds; in this case, the triphenylcarbinol and pyrazolone azo dye were formed.

EXPERIMENTAL

1-Phenyl-3-methyl-4-triphenylmethylpyrazolone-5

1.95 g of triphenylcarbinol and 1.50 g of 1-phenyl-3-methylpyrazolone-5 were dissolved in 10 ml of glacial acetic acid, to which had been added beforehand 3 drops of concentrated hydrochloric acid. The resulting solution was boiled for 3 hours in a flask with reflux condenser. After cooling, there precipitated from the solution a precipitate which was filtered and then dried. The precipitate was boiled with 40 ml of alcohol. After cooling, the portion which did not dissolve in alcohol was filtered and dried. 0.95 g of substance with m.p. 208 - 210° resulted. The compound obtained was dissolved in 40 ml of a 0.3% alcoholic solution of potassium hydroxide. Upon acidification of the resulting solution with acetic acid, a precipitate formed which was filtered and dried. 0.90 g of substance, with m.p. 209 - 211° resulted. A second precipitation of the compound, as well as recrystallization from alcohol, did not result in any increase of the melting point.

0.1162 g substance: 0.3408 g CO_2; 0.0606 g H_2O. 0.1102 g substance: 6.7 ml N_2 (20°, 758 mm).
Found %: C 83.30; H 6.07, N 7.01. $C_{29}H_{24}ON_2$. Calculated %: C 83.60; H 5.81; N 6.73.

1-Phenyl-3-methyl-4-triphenylmethyl-5-acetoxypyrazole

3.00 g of 1-phenyl-3-methylpyrazolone-5 and 3.90 g of triphenylcarbinol were dissolved in 20 ml of acetic anhydride, to which 5 drops of concentrated hydrochloric acid had been added beforehand. The resulting solution was heated for 3 hours on an oil bath (bath temperature 150 - 160°). Upon cooling there resulted a crystalline white precipitate from the solution, which was filtered and dried. 5.67 g of substance with m.p. 234° resulted. The yield was 88.4% of theory. The m.p. was 236° after recrystallization from alcohol or benzene.

0.1973 g substance: 10.4 ml N_2 (22°, 764 mm). 0.1992 g substance: 10.5 ml N_2 (20°, 763 mm).
Found %: N 6.07, 6.11. $C_{31}H_{26}N_2O_2$. Calculated %: N 6.10

0.1 g of 1-phenyl-3-methyl-4-triphenylmethylpyrazolone-5 was dissolved in 5 ml of acetic anhydride, to which one drop of concentrated hydrochloric acid had been added beforehand. The reulting solution was heated for 3 hours on an oil bath (bath temperature 150 - 160°). The reaction mixture was poured into water, and on the following day the precipitate which had formed was filtered off. The melting point of the resulting compound was 234 - 236°. A sample mixed with 1-phenyl-3-methyl-4-triphenylmethyl-5-acetoxypyrazolone (m.p. 236°) melted at 234 - 236°.

1-Phenyl-3-methyl-4-(9'-phenyl-10'-methyl-9',10'-dihydroacridyl-9')-pyrazolone-5.

1.42 g of 9-phenyl-9-hydroxy-10-methyl-9,10-dihydroacridine (0.005 mole) and 0.87 g of 1-phenyl-3-methylpyrazolone-5 (0.005 mole) were dissolved in 40 ml of alcohol, and the resulting solution was boiled for 20 minutes on a water bath. The precipitate formed was filtered off, washed with alcohol, and dried. 1.95 g of substance, with m.p. 188°, was obtained. After crystallization from alcohol, the melting point of the compound obtained remained unchanged Yield was 88.7% of theory.

0.1400 g substance: 0.4180 CO_2; 0.0723 H_2O. 0.1206 g substance: 10.0 ml N_2 (24°, 763 mm).
Found %: C 81.43; H 5.78; N 9.47. $C_{30}H_{25}ON_3$. Calculated %: C 81.26; H 5.69; N 9.48.

0.44 g of 1-phenyl-3-methyl-4-(9'-phenyl-10'-methyl-9',10'-dihydroacrid yl-9')-pyrazolone-5 (0.001 mole) and 1 g of sodium acetate were dissolved in 12 ml of glacial acetic acid. 5 ml of 0.2M solution of p-nitrophenyldiazonium chloride was added to the resulting solution. A dye precipitate formed immediately, which was filtered off and dried. 0.25 g of azo dye was obtained, which, after recrystallization from glacial acetic acid, melted at 198°. A mixed sample of the azo dye obtained with that resulting from interaction of 1-phenyl-3-methylpyrazolone-5 with p-nitrophenyldiazonium (m.p. 198°), melted at 198°.

The acetate filtrate was mixed with 100 ml of 20% potassium hydroxide solution. The precipitate which formed was filtered off, washed with water and dried. 0.25 g of substance with m.p. 135 - 136° resulted A sample of the obtained compound when mixed with 9-phenyl-9-hydroxy-10-methyl-9,10-dihydroacridine (m.p. 140°), melted at 136°.

Upon reacting p-nitrophenyldiazonium with 1-phenyl-3-methyl-4-triphenylmethylpyrazolone-5, with 1-phenyl-3-methyl-4-(p-dimethylaminotriphenylmethyl)pyrazolone-5, with 1-phenyl-3-methyl-4-(p,p'-tetramethyldiaminotriphenylmethyl)-pyrazolone-5, and with 1-phenyl-3-methyl-4-(p,p',p"-hexamethyltriaminotriphenylmethyl)-pyrazolone-5, respectively, the corresponding triphenylcarbinols, and the pyrazolone dye, were formed.

1-Phenyl-3-methyl-4-(p,p',p"-hexamethyltriaminotriphenylmethyl)-pyrazolone-5.

2.01 g of the methyl ester of 4,4',4"-hexamethyltriaminotriphenylcarbinol (0.0005 mole) and 0.87 g of 1-phenyl-3-methylpyrazolone-5 (0.0005 mole) were dissolved in 15 ml of benzene, and the resulting dark-violet solution boiled for 1 hour After cooling, 120 ml of gasoline was added to the benzene solution. A precipitate formed, which was filtered off and dried. 0.9 g, with m.p. 154 - 156° resulted.

0.0712 g substance: 8.2 ml N_2 (25°, 750 mm), 0.1136 g substance: 12.8 ml N_2 (24°, 756 mm).
Found %: N 12.87, 12.74. $C_{35}H_{39}ON_5$. Calculated %: N 12.84.

SUMMARY

1. Triphenylcarbinol enters into a condensation reaction with 1-phenyl-3-methylpyrazolone-5- under more rigorous conditions than for 9- hydroxy-9-phenyl-10-methyl-9,10-dihydroacridine or the methyl ester of 4,4',4"-hexamethyltriaminotriphenylcarbinol.

2. Upon reacting diazo compounds with condensation products of triarylcarbinols and with 1-phenyl-3-methyl-pyrazolone-5, there are formed triarylcarbinol and pyrazolone azo dyes.

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* See Consultants Bureau Translation, page 1103.

off and dried, 0.89 g of the dye was obtained, which, [illegible] melted at [illegible]. A mixed sample of the acid dye obtained with [illegible] (m.p. 188°) [illegible]

The mother filtrate was mixed with [illegible]. The [illegible] which formed was filtered off, washed with water and dried. [illegible] A sample of the obtained compound when mixed with [illegible] melted at 139°.

[illegible] phenyl-3-methyl-4-(p-dimethylaminophenylazo)-[illegible] dimethylaminophenyl)-[illegible] methyl)-pyrazolone-5, respectively, [illegible]

1-Phenyl-3-methyl-4-[illegible]-pyrazolone-5

2.0 g of the methyl [illegible] was heated for 1 hour. After cooling, [illegible] which was filtered off and dried, [illegible]

Found %: N [illegible]. Calculated %: N [illegible].

SUMMARY

1. Triphenylcarbinol enters into a condensation reaction with [illegible] conditions than [illegible] hexamethyltriaminotriphenylcarbinol.

2. Upon reacting dyes [illegible] pyrazolones, [illegible]

LITERATURE CITED

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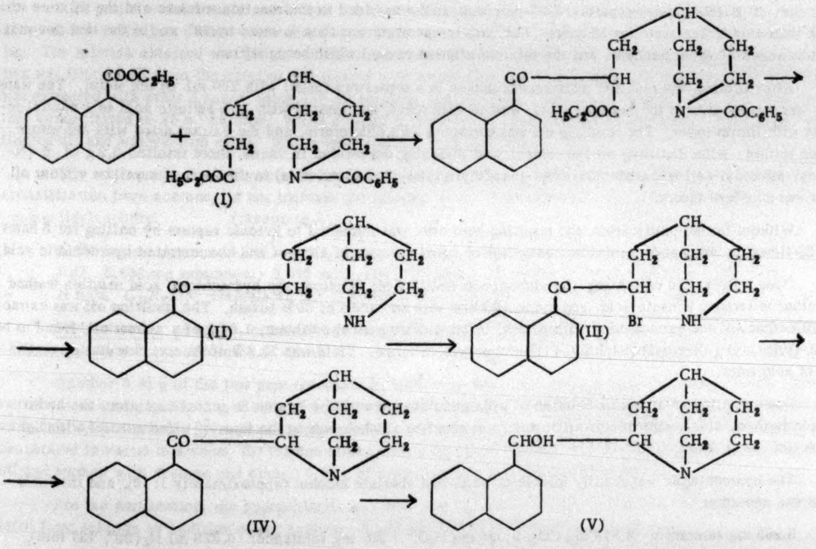
* See Consultants Bureau Translation, page 1123.

[QUINUCIYDYL-(2)]-[NAPHTHYL-(1)]-CARBINOL. VII.

V. M. Rubtsov and V. A. Volskova

A study of hydroquinine and its pyridine analogs [1] has indicated that the activity of compounds of the quinine-type alkaloids is related not so much to the quinoline nucleus as to the position of the quinuclidic radical in this ring. Thus, for example, rearrangement of the quinoeuclidic radical to the number 2 or 8 position of the quinoline ring results in a loss of chemotherapeutic action, at the same time that replacement of the quinoline ring by the corresponding pyridine ring (pyridyl-4) affects but little the chemotherapeutic index. Hence, the presence of a quinoline ring is not strictly required for exhibiting antimalarial action in compounds of this type, and by appropriate selection of another radical, active preparations can be obtained.

This concept has served as the basis for synthesizing [quinuclidyl-(2)]-[naphthyl-(1)]-carbinol, which was synthesized according to the following scheme:



Upon condensing the ethyl ester of α-naphthoic acid and the ethyl ester of β-[N-benzoylpiperidyl-(4)]-propionic acid, there resulted the keto ester (I). The reaction proceeded less readily than with the corresponding quinoline derivatives, and the yield of keto ester did not exceed 24%. Saponification of the keto ester with 17% hydrochloric acid gave unsatisfactory results; reaction proceeded readily only when a mixture consisting of equal volumes of alcohol and of concentrated hydrochloric acid was used. [β-(Piperidyl-(4))-ethyl]-[naphthyl-(1)]-ketone (II) which resulted in this case was in the form of a yellow oil, forming a crystalline hydrochloride with m.p. 173.5 - 175°, when mixed with an alcoholic solution of hydrogen chloride. This compound, when treated with bromine in 48% hydrobromic acid, converted into the bromoketone (III), which cyclized readily upon reacting with sodium bicarbonate, to form [quinuclidyl-(2)]-[naphthyl]-(1)]-ketone (IV). Reduction of the carbonyl group to carbinol was carried out by hydrogenation of the ketone hydrochloride in aqueous medium in the presence of palladium black. From the hydrogenation product, which represented a mixture of four stereoisomeric carbinols (V), two diastereoisomeric racemates were isolated, whose properties are given in the Table.

Racemate	Base	Hydrochloride	Characteristic
A	White needles, m.p. 200 - 201°	White crystalline powder, m.p. 203.5 - 205.5°	Base very poorly soluble in ether
B	White prisms, m.p. 63 - 65°	White crystalline powder, m.p. 267.5 - 269°	Base readily soluble in ether

The racemates obtained, in contrast to the quinic alkaloids, did not change when boiled with 50% acetic acid.

Both racemates were found to be inactive when tested on green finches infected with Plasmodium relictum

EXPERIMENTAL

[β-(Piperidyl-(4))-ethyl]-[naphthyl-(1)]-ketone (II).

10 g of the ethyl ester of α-naphthoic acid was added to sodium ethylate obtained from 1.23 g of powdered metallic sodium and 2.46 g of absolute alcohol in an absolute ether medium. The mixture was slowly heated on an oil bath to 100°, with simultaneous distilling off of the ether. When the bath temperature rose to 100°, 8.5 g of the ethyl ester of β-[N-benzoyl-piperidyl-(4)]-propionic acid was added to the reaction mixture and the mixture stirred at the indicated temperature for 19 hours The bath temperature was then lowered to 70°, andto the reaction mixture was added 50 ml of benzene, and the mixture allowed to cool while being stirred.

After cooling, the reaction mixture was shaken in a separatory funnel with 200 ml of ice water. The water layer was separated from the benzene layer, washed with ether, and treated with 10% sulfuric acid to a neutral reaction with litmus paper. The resulting oil was extracted with chloroform, and the extract dried with anhydrous sodium sulfate. After distilling off the solvent, and removing the residue in vacuo, there resulted 3.2 g of β-[N-benzoyl-piperidyl-(4)]-α-carboethoxyethyl-[naphthyl-(1)]-ketone (keto ester) in the form of a yellow viscous oil. Yield was 23.6% of theory.

Without further purification, the resulting keto ester was subjected to ketonic rupture by boiling for 3 hours with 20 times the amount of a mixture consisting of equal volumes of alcohol and concentrated hydrochloric acid.

Upon termination of heating, the alcohol was distilled off in vacuo, the hydrochloric acid solution washed with ether to remove benzoic acid, and made alkaline with an excess of 50% potash. The resulting oil was extracted with ether and the extract dried with potash. After distilling off the solvent, 1.84 g of a yellow oil, found to be the [β-(piperidyl-(4))-ethyl]-[naphthyl-(1)]-ketone was obtained. Yield was 73.8% of theory, calculating on the basis of keto ester.

Upon reacting an alcoholic solution of hydrogen chloride with the ketone in acetone solution, the hydrochloride formed, which, after recrystallization from absolute alcohol, was in the form of white needles with light yellow tint. M.p. 173.5 - 175°.

The hydrochloride was readily soluble in water and absolute alcohol (approximately 1:10), and insoluble in acetone and ether.

3.295 mg substance: 8.579 mg CO_2; 2.095 mg H_2O. 7.815 mg substance: 0.323 ml N_2 (20°, 737 mm). Found %: C 71.01; H 7.11; N 4.66. $C_{18}H_{21}ON \cdot HCl$. Calculated %: C 71.14; H 7.30; N 4.61.

Hydrobromide of [β-(piperidyl-(4))-α-bromoethyl]-[naphthyl-(1)]-ketone (III)

1.03 g of bromine in 10 ml of 48% hydrobromic acid was added to a solution of 1.97 g of piperidylethylnaphthylketone hydrochloride in 12 ml of 48% hydrobromic acid heated at 70°, over a period of 10 minutes with stirring. The temperature was then increased to 80°, and stirring continued for another 25 minues. Upon cooling, a precipitate formed, which was filtered off, washed with water, acetone, and dried in the air; yellow, crystalline powder, melting at 189 - 190°. Readily-soluble in chloroform, poorly so in water; insoluble in acetone and ether. Yield was 2.45 g (88.4%).

7.119 mg substance: 6.272 mg AgBr. 6.703 mg substance: 5.899 mg AgBr. Found %: Br 37.48, 37.45. $C_{18}H_{20}ONBr \cdot HBr$. Calculated %: Br 37.43.

[Quinuclidyl-(2)]-[naphthyl-(1)]-ketone (IV).

2.3 g solution of β-[piperidyl-(4)]-α-bromoethyl-[naphthyl-(1)]-ketone hydrobromide in 30 ml of chloroform was mixed with 2.5 g solution of sodium bicarbonate in 30 ml of water. The mixture was shaken for 2.5 hours. The chloroform layer was then separated from the water layer and dried with potash. After evaporation of the chloroform, the residue was recrystallized frompetroleum ether. 0.86 g of quinuclidylnaphthylketone resulted in the form of white, prismatic platelets of yellow tint, melting at 98.5 - 100°. Yield was 60% of theory.

The substance was readily-soluble in alcohol, chloroform, ether and acetone; soluble in hot petroleum ether, insoluble in water.

4.076 mg substance: 12.133 mg CO_2; 2.624 mg H_2O. 5.783 mg substance: 0.282 ml N_2 (17.5°, 733.8 mm). Found %: C 81.18; H 7.20; N 5.52. $C_{18}H_{19}ON$. Calculated %: C 81.46; H 7.22; N 5.28.

Hydrochloride – white platelets (from water), m.p. 246 - 247°; readily soluble in alcohol and chloroform, soluble in water, insoluble in acetone and ether.

6.905 mg substance: 3.316 mg AgCl. Found %: Cl 11.88. $C_{18}H_{19}ON \cdot HCl$. Calculated %: Cl 11.76.

[Quinuclidyl-(2)]-[naphthyl-(1)]-carbinol (V)

1.62 g of the above-obtained ketone was dissolved in 6.19 ml of 1N hydrochloric acid and 30 ml of water. 10 ml of 2 % palladium chloride was added to the solution; a pink precipitate resulted which dissolved upon shaking. The solution obtained was hydrogenated at room temperature. After completion of hydrogenation, the solution was filtered off from the catalyst and treated with excess 50% potassium hydroxide solution. The resulting base was extracted with ether 4 times, using 125 ml portions, and the extract dried with potash. The ether solution was then concentrated to 25 ml volume. White crystals in the form of white needles precipitated. The crystals were filtered off and washed with ether. 0.37 g was obtained; m.p. 200 - 201°.

The substance was readily soluble in alcohol and acetone, very poorly in ether, insoluble in water. Recrystallization from acetone did not increase the melting point. This substance, according to analysis, was the quinuclidylnaphthyl (racemate A).

3.400 mg substance: 10.143 mg CO_2; 2.339 mg H_2O. 2.828 mg substance: 8.380 mg CO_2; 2.004 mg H_2O. 8.136 mg substance: 0.372 ml N_2 (24°, 728 mm). Found %: C 80.82, 80.81; H 7.70, 7.92; N 5.03. $C_{18}H_{21}ON$. Calculated %: C 80.85; H 7.84; N 5.24.

Hydrochloride. A white, crystalline powder, with m.p. 203.5 - 205.5°. Readily soluble in water, alcohol, chloroform and acetone; insoluble in ether.

Another 0.08 g of the less pure racemate A, with m.p. 194 - 197° resulted from the mother liquor upon additional evaporation, and 1.08 g of a light-yellow oil, readily soluble in ether. The oil was mixed with a calculated amount of 14% alcoholic hydrogen chloride solution, calculated on the basis of hydrochloride. The mixture was evaporated in vacuo to dryness, the residue mixed with 4 ml of dry acetone, and the resulting precipitate filtered off and washed with acetone and ether. 0.92 g of hydrochloride, melting at 249 - 251° resulted.

For the purification, the hydrochloride was dissolved in a small volume of absolute alcohol, and was isolated from solution by addition of dry acetone. Yield was 0.6 g.

Hydrochloride. A white, crystalline powder with m.p. 267.5 - 269°. Readily-soluble in water, alcohol, chloroform; insoluble in dry acetone and ether According to analysis, this substance was found to be the quinuclidylnaphthylcarbinol hydrochloride (Racemate B hydrochloride).

3.037 mg substance: 7.919 mg CO_2; 2.006 mg H_2O. 3.700 mg substance: 9.672 mg CO_2; 2.386 mg H_2O. 7.136 mg substance: 0.314 ml N_2 (24°, 728 mm). Found %: C 71.11, 71.29; H 7.38, 7.21; N 4.84. $C_{18}H_{21}ON \cdot HCl$. Calculated %: C 71.14; H 7.30; N 4.61.

The free base was isolated from the hydrochloride as a colorless oil which crystallized after standing 2 days in a vacuum desiccator over potassium hydroxide. Melting point of the crystals was 63 - 65°. The base was readily soluble in alcohol, acetone, ether and chloroform.

The resulting diastereoisomeric racemates A and B, in contrast to the quinic alkaloids, do not change with boiling in 50% acetic acid.

SUMMARY

1. [Quinuclidyl - -(2)]-[naphthyl-(1)]-ketone has been synthesized.

2. Upon catalytic hydrogenation of the indicated ketone, there is formed a mixture of two diastereoisomeric racemates, which have been separated by virtue of their differential solubility in ether.

3. The racemates obtained, in distinction to the quinic alkaloids, do not change when boiled with 50% acetic acid

4. Both racemates have been found inactive when tested on green finches infected with Plasmodium relictum.

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RELATIONSHIP BETWEEN THE QUANTITY OF HYDROGEN BROMIDE EVOLVED AND THE STRUCTURES OF BROMINATED OLEFINS

A. A. Petrov

In determining the degree of unsaturation for hydrocarbons by the volume of bromine added, a certain amount of hydrogen bromide ("abnormal bromination") is usually formed. Despite the fact that many works have been devoted to problems of halogenation of unsaturated compounds, quantitative data have nevertheless been very few regarding the formation of hydrogen halide acids in relation to the initial unsaturated hydrocarbon. Thus, V. I. Esafov [1] investigated bromination of certain dienes, wherein he noted formation of a larger amount of hydrogen chloride than upon bromination of olefins.

In the present work, there have been investigated a large number of cases relating the quantity of hydrogen bromide evolved to the structure of brominated olefins. Bromination was carried out with 1% Br solution in methanol, saturated with NaBr. Bromination, as carried out above, almost excludes the possibility of hydrogen bromide evolution by substitution reaction [2]. Data obtained on formation of hydrogen bromide, given in mol per cent hydrogen bromide, are related to the quantity of bromine used, and are presented in the Table.

Hydrocarbon (Group I)	HBr (mol %)	Hydrocarbon (Group II)	HBr (mol %)	Hydrocarbon (Group III)	HBr (mol %)
Hexene-1	16.1	2-Methylpentene-2	29.4	2,4-Dimethylpentene-2	42.2
Heptene-1	16.4	3-Methylpentene-2	29.2	3,4-Dimethylhexene-2	40.3
Octene-1	16.3	2-Methylhexene-2	30.4	2,4-Dimethylhexene-4	53.6
Nonene-1	16.4	3-Methylhexene-3	29.3	2,4,4-Trimethylpentene-1	46.0
Decene-1	16.9	3-Ethylpentene-2	27.5	2,2,3-Trimethylpentene-3	44.0
Dodecene-1	15.6	4-Methylheptene-3	30.7	2,3,4-Trimethylpentene-2	75.0
Tridecene-1	15.8	2-Ethylhexene-1	29.2	2,2,3-Trimethylhexene-3	41.5
Hexadecene-1	17.0	3-Ethylhexene-2	29.5	Triisobutylene	60.3
Heptene-3	15.5	5-Methylnonene-4	28.5	1-Cyclohexylcyclohexene-1	55.0
Nonene-4	15.1	4-Propylheptene-3	34.0		
Cyclohexene	16.7	2,3-Dimethylbutene-2	29.6		
3-Methylcyclohexene-1	18.8	2,5-Dimethylhexene-2	28.2		
Allylcyclohexane	16.5	2,3,3-Trimethylbutene-1	26.1		
Allylbenzene	10.0	1-Methylcyclohexene-1	26.3		
4-Methylpentene-1	16.1	1-Ethylcyclohexene-1	26.1		
5-Methylhexene-1	14.0	1-Propylcyclohexene-1	28.3		
6-Methylhexene-1	14.9	1-Butylcyclohexene-1	29.4		
3,3-Dimethylbutene-1	14.0	1-Methylcyclopentene-1	40.0		
4,4-Dimethylpentene-1	17.8	1-Ethylcyclopentene-1	40.2		
4,4-Dimethylhexene-1	18.7	1-Butylcyclopentene-1	38.5		

Note. The data given do not take into account hydrogen bromide in the original solution.

As can be seen from data given in the Table, unsaturated hydrocarbons can be divided into three groups; differing in the amount of hydrogen bromide evolved during bromination. The first group consists of hydrocarbons, linear in structure, as well as branched hydrocarbons with the alkyl side chain isolated from the double bond. Here too, belong cyclic hydrocarbons with analogous distribution of the multiple bonds. For this overall group of hydrocarbons, a small and approximately equal (for each olefin) volume of hydrogen bromide evolution is characteristic, fluctuating within the range 14 - 16 mol %. The second group consists of hydrocarbons with branching at the position of the double bond, i.e., hydrocarbons with a tertiary double bond, polarized, and already possessing known steric hindrance To this group are also related the cycloolefins which have an analogous structure. For all hydrocarbons of the second group, the approximately equal formation of hydrogen bromide is characteristic, fluctuating in the range 27 - 29% (for the five-membered cyclenes, in the range 38-40%). Finally, a third group of hydrocarbons is characterized by considerably greater evolution of hydrogen bromide. To this group belong the branched hydrocarbons with one part of the tertiary bond groups creating steric hindrance (isopropyl, sec.-butyl, ter.-butyl). There is no clear-cut mechanism as to the amount of hydrogen bromide evolved when hydrocarbons of this group are brominated, since the amount of hydrogen bromide formed fluctuates within a rather large range (from 41 to 75 mol %).

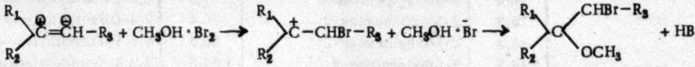
The rather considerable difference in amount of hydrogen bromide evolved upon bromination of hydrocarbons of Groups I and II makes it possible to solve the reverse problem: according to the amount of hydrogen bromide evolved, the content of olefin with tertiary double bond among the products that brominate is calculated. Experiments carried out with synthetically-prepared olefin mixtures of normal structure, and olefins with a tertiary double bond, have indicated that hydrogen bromide evolution is in proportion to the content of branched hydrocarbons in the mixture. It is understood that the presence of olefins with a tertiary group may distort considerably the analytical results.

To conclude, we shall consider the reaction mechanism for hydrogen bromide formation. There are indications in the literature that upon brominating with a methanol solution of bromine, aside from the usual halogen addition at the double bond, there also proceeds an abnormal bromination reaction, with formation of methoxymonobromides of the initial hydrocarbon [3, 4, 5].

The author also found methoxymonobromides among the bromination products.

Since formation of hydrogen bromide and methoxybromide proceeds with particular intensity upon bromination of olefins with tertiary double bonds, the author was therefore attracted to the use of a known scheme for chlorination of tertiary olefins according to Lvov-Tishchenko [6, 7] for a clarification of the bromination mechanism. Considering that the halogenating agent in the author's case is a molecular compound of bromine and methyl alcohol, and not of bromine alone, the bromination reaction can be represented on the whole as follows:

$$\text{I)}\quad R_1{-}CH{=}CH{-}R_2 + CH_3OH\cdot Br_2^{*} \longrightarrow R_1{-}CHBr{-}CHBr{-}R_2 + CH_3OH;$$

II) 

$$\text{II)}\quad (R_1)(R_2)\overset{\oplus}{C}{=}\overset{\ominus}{C}H{-}R_3 + CH_3OH\cdot Br_2 \longrightarrow (R_1)(R_2)\overset{+}{C}{-}CHBr{-}R_3 + CH_3OH\cdot\overset{-}{Br} \longrightarrow (R_1)(R_2)C(CHBr{-}R_3)(OCH_3) + HBr.$$

First of all, the initial hydrocarbon does not possess branching at the double bond, and hence polarization of the molecule is negligible, and the predominant direction for the bromination reaction is the usual addition of bromine at the double bond (classical scheme).

In the second case, the brominated olefin has a tertiary double bond, and hence the hydrocarbon molecule is polarized. Therefore, in this case, as well as with chlorination according to the Lvov-Tishchenko reaction, halogen addition is noted as deviating from the classical addition scheme, and also, in contrast to chlorination, proceeds almost quantitatively along the abnormal route, the extent of abnormal reaction in the given case depending entirely upon the structure of the hydrocarbon brominated, and, as has already been mentioned, fluctuating within the range 25 - 75% (see Table).

It is quite characteristic that the value for abnormal bromination increases noticeably in those cases where, in the hydrocarbon molecules, there are present radicals attached to the multiple bond, thus creating steric hindrance. Because of the fact that the quantity of evolved hydrogen bromide, and hence also the quantity of hydrocarbon which is reacting abnormally, also increases in that case where the radical which is creating steric hindrance is located at a negatively polarized carbon atom, it might be assumed, therefore, that steric hindrance (branching at the multiple bond) inhibits for the most part normal addition of halogens, which, therefore, favors bromination according to scheme (II).

EXPERIMENTAL

The hydrocarbons used were prepared synthetically by the Grignard reaction, with subsequent dehydration of the alcohols, and according to the Grignard-Wurtz reaction. The conditions of synthesis, and the constants for the resulting hydrocarbons, were published earlier by the author [8].

The solution for bromination was prepared by addition of 3 - 4 ml of bromine to 1 liter of methanol saturated with sodium bromide. By maintaining the above indicated conditions, the ratio of hydrogen bromide to

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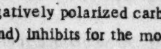
* Electronic:



$$\left[CH_3:\underset{\textstyle H}{\overset{\cdot\cdot}{O}}:\overset{\cdot\cdot}{\underset{\cdot\cdot}{Br}}:\right]^{+}\overset{-}{Br}$$

free bromine in the initial solution does not exceed 0.5-1 mol %. With prolonged storage of the solution, the amount of hydrobromic acid in it may increase somewhat (up to 2 %), and accurate data therefore, upon analysis of the hydrocarbon mixtures, can be obtained only when the hydrobromic acid contained in the initial solution is taken into account.

The procedure for determination of hydrogen bromide formed by bromination of olefins is close to the procedure for determination of bromine numbers according to Kaufman [2].

A measured volume (0.1 - 0.5 ml) of the hydrocarbon to be investigated was added to 20 ml of bromine solution. After addition of 10% aqueous potassium iodide solution, and one-minute standing, the excess bromine was titrated with thiosulfate. After decolorization, 20ml of 5% potassium iodate was added to the flask, and the precipitated iodine filtered off a second time. Experimental data indicated that the hydrogen bromide formation reaction and the bromine addition proceed quite rapidly, and that one-minute standing of the hydrocarbon investigated in the bromine solution suffices.

Investigation of the bromination products was carried out by the author, using as an example, 2,5-dimethylhexene-2. The bromides resulted from slow addition of the hydrocarbon to 1 liter of bromine solution to the point of complete decolorization of the latter. The methanol solution of bromides obtained in this manner was diluted with water, and the bromides were then extracted with ether. After evaporation of the main ether volume (in an open beaker), the residue was dried with $CaCl_2$ and blown in vacuo (10 mm) with nitrogen for complete removal of the hydrocarbon, methanol and ether residues. Products resulting from these procedures were colorless and possessed the following properties:

n_D^{20} 1.4860; d_4^{20} 1.3300.

Found %: C 42.50, 42.38; H 7.06, 6.99; O 3.8, 4.2; Br 46.4, 46.6 (Carius); OCH_3 6 (Zeisel)

SUMMARY

1. Bromination of unsaturated hydrocarbons with a Kaufman solution has been investigated.

2. It has been shown that the amount of hydrogen bromide evolved in this case depends upon the structure of the olefins brominated, and increases in the following order: olefins with primary-secondary double bond < olefins with tertiary double bond < olefins with tertiary double bond and radicals creating steric hindrance.

3. A bromination scheme explaining the results has been proposed.

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U.S.S.R.

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* See Consultants Bureau Translation, page 1813.

[illegible] bromine in the [illegible] solution [illegible] water. With prolonged [illegible] of the [illegible], the amount of hydrobromic acid in it [illegible] of the hydrocarbon [illegible] reaction may occur.

The procedure for determination of hydrogen bromide [illegible] by a combination of [illegible] in the procedure for determination of bromine numbers according to [illegible] [3].

A measured volume [illegible] of the [illegible] bromine solution. After addition of 10% [illegible] potassium iodide [illegible] was titrated with thiosulfate [illegible] was placed in the flask, and the unsaturated [illegible] and the bromine addition [illegible] figured in the bromine solution used.

Investigation of the bromination product was carried out [illegible] scheme 3. The [illegible] resulted from the [illegible] of the hydrocarbon [illegible] of bromine [illegible] of complete decolorization of the latter. The [illegible] with water, and the [illegible] were then extracted with [illegible] open beaker, the residue was dried with $CaCl_2$ and [illegible] of the hydrocarbon, [illegible] and had the following properties:

[illegible]

Found %: C [illegible] H [illegible]

[illegible]

1. Bromination of unsaturated hydrocarbons with a [illegible].

2. It has been shown that the amount of hydrogen bromide [illegible] depends on the structure of the olefins brominated, and increases in the following [illegible]: olefins with [illegible] double bond < olefins with tertiary double bond < [illegible].

3. A [illegible] the results has been proposed.

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[1] V. I. Esafov, J. Gen. Chem. 17, 1453 (1947).

[2] C. D. [illegible] and [illegible]

[3] [illegible]

[4] [illegible]

[5] [illegible], J. Am. Chem. Soc. 74, [illegible]

[6] [illegible]

[7] [illegible]

[8] [illegible]

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* See Consultants Bureau Translation, page [illegible].

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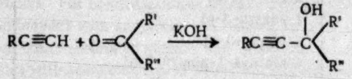
DERIVATIVES OF ACETYLENE. 160. CONDENSATION OF ALDEHYDES AND KETONES WITH ACETYLENE UNDER PRESSURE

A NEW PROCEDURE FOR SYNTHESIS OF ACETYLENIC ALCOHOLS

I. N. Nazarov, I. L. Kotlyarevsky and V. F. Ryabchenko

Of the described synthetic procedures for acetylenic alcohols, the simplest method is that of A. E. Favorsky [1], which consists of condensing acetylene with ketones under the influence of powdered potassium hydroxide:



With all of its advantages, however, this method has a number of significant disadvantages which limit its range of usefulness. In particular, the Favorsky method is inapplicable to the synthesis of secondary acetylenic alcohols by the condensation of acetylene with aldehydes [2, 3]. Directions for synthesis of secondary acetylenic alcohols, according to the Favorsky method, are to be found for the most part in the patent literature [4, 5, 6, 7], where conditions for reaction, and yields of secondary alcohols, are not given. Special attention is given in these works to solvents, for which role acetals, ethylene glycol esters and diethylene glycol, as well as hydrocarbons boiling above 100°, are proposed.

The most wide-spread synthetic procedure for secondary acetylenic alcohols is the method of Iotsich [8], which gives good alcohol yields, however, only when starting with monosubstituted acetylene, the method being based upon condensation of aldehydes with acetylenides of an alkali metal in liquid ammonia, which presents inconveniences associated with use of large quantities of liquid ammonia.

The great drawback of the latter procedure is its exceptional sensitivity to moisture, the presence of which lowers sharply the yields of acetylenic alcohols [9]. The method of synthesizing secondary acetylenic alcohols under the influence of sodamide and potassium hydroxide mixture [10], published in 1945, suffers from the same disadvantage.

Research carried out for several years in the authors' laboratory in the field of acetylenic alcohol reactions, made it necessary to develop a simple synthetic method for acetylenic alcohols which would excel in simplicity, in accurate reproducibility of results, and produce sufficiently high yields.

Having studied the Favorsky reaction, the authors concluded that it proceeds according to metalloorganic mechanism by formation of potassium acetylenide [11]. By studying its kinetics [12], Korotkov and Parfenova also arrived at the same conclusion regarding the mechanism for this reaction. The authors observed that the solubility of acetylene in ether increases markedly upon addition of potassium hydroxide to the ether Considering this phenomenon to be associated with the formation of potassium acetylenide, the authors decided to investigate the Favorsky reaction course under acetylene pressure, assuming that the pressure would promote displacement of the $HC\equiv CH + KOH \rightleftharpoons HC\equiv CK + H_2O$ equilibrium in the direction of potassium acetylenide formation, and consequently to formation of conditions favorable to condensation of acetylene with carbonyl compounds. There is given in the literature only one brief patent direction for the Favorsky reaction carried out under pressure [13], and there attention is paid to this simply to decrease condensation of acetone itself under the influence of potassium hydroxide.

The authols method for carrying out the Favorsky reaction consists of the following: pulverized potassium hydroxide is charged into a metallic reactor (see below), along with ether dried over calcium chloride. The mixture is saturated with acetylene under 5 - 10 atmospheres, with vigorous stirring, the pressure being maintained during the entire course of reaction. Aldehyde or ketone is then added at a uniform rate from a dropping funnel, working under pressure, into the reactor, with vigorous stirring. Stirring is continued for an additional 20-30 minutes, after which pressure is released and the reaction mixture treated with water taken in equal or double amount according to the weight of alkali. The product is then neutralized with carbon dioxide, extracted with ether, dried with potash and fractionated. The crude acetylenic alcohol, after the first fractionation, was dried with potash and fractionated on a column with 25 theoretical plates, whose effectiveness was measured at the height of irrigation.

Working in accordance with this method, the secondary and tertiary acetylenic alcohols given in the Table were obtained.

Expt. No.	Aldehyde or ketone	Acetylenic alcohol	Yield of pure alcohol (%)	
			Without presence of aliphatic alcohols	In the presence of aliphatic alcohols
1	Acetaldehyde	1-Butyn-3-ol	20	43
2	Propionic aldehyde	1-Pentyn-3-ol	36	45
3	n-Butyric aldehyde	1-Hexyn-3-ol	51.5	59
4	Iso-butyric aldehyde	4-Methyl-1-pentyn-3-ol	47.5	50
5	Hydrocinnamic aldehyde	5-Phenyl-1-pentyn-3-ol	37.7	54.5
6	Enanthol	1-Nonyn-3-ol	51.5	–
7	Isovaleric aldehyde	5-Methyl-1-hexyn-3-ol	74.5	–
8	Acetone	3-Methyl-1-butyn-3-ol	93	–
9	Methylethyl ketone	3-Methyl-1-pentyn-3-ol	80	–
10	Diethyl ketone	3-Ethyl-1-pentyn 3-ol	82	–
11	Di-n-propyl ketone	3-Propyl-1-hexyn-3-ol	70	–
12	Isobutyrone	3-Isopropyl-4-methyl-1-pentyn-3-ol	–	65
13	Cyclohexanone	1-Ethynyl-1-cyclohexanol	96.7	–
14	Cyclopentanone	1-Ethynyl-1-cyclopentanol	–	42
15	Acetophenone	3-Phenyl-1-butyn-3-ol	–	70
16	Mesityl oxide	3,5-Dimethyl-4-hexen-1-yn-3-ol	–	5.2

With further study, it was found that the yield of acetylenic alcohols increases considerably with a mixture of potassium hydroxide and ether containing a small amount of aliphatic alcohols, the most effective among which were found to be ethanol and n-butanol. The yield of acetylenic alcohols obtained by condensation of aldehydes and ketones with acetylene under pressure in the presence of small additions of ethanol or of n-butanol are given in the last column of the Table.

The procedure described makes it possible also to effect condensation of acetylene with cyclopentanone, acetophenone and mesityl oxide, which were heretofore, impossible to combine. An attempt to condense carbon dioxide with acetylene by this procedure gave only traces of propiolic acid. Negative results were obtained when attempting to condense acetylene with paraform, acrolein and benzaldehyde.

EXPERIMENTAL

Description of the Reactor for Condensing Aldehydes and Ketones Under Pressure

Condensation of aldehydes and ketones with acetylene under pressure was carried out in a steel reactor of 1 liter volume, tested for 50 atmospheres, equipped with a jacket for water or brine cooling and with a propeller stirrer for 500 - 1000 revolutions/minute. The body of the reactor had a flat collar with a lead sealer. Bolts were threaded into the collar to fasten down the lid which contained two special doors for charging reactants, a tripod and manometer, greasing stick for lubricating the stirrer gasket, two gas inlet tubes and one gas outlet tube for reducing pressure. A connecting pipe screwed into a sleeve was connected to the bottom of the reactor. Such an arrangement permitted charging and discharging without removing the lid. The reactor had a steel dropping funnel of 200 ml volume, through which was fed by liquid pump into the reactor at a uniform rate either aldehyde or ketone, and acetylene entered the reactor at a given pressure via the gas connecting tube.

Description of the Synthetic Method for Acetylenic Alcohols, Using Pressure

Dry ether was charged into the above-described steel reactor, powdered potassium hydroxide, and if needed, a small amount of alcohol added. The air was displaced from the reactor by nitrogen, using two washings with the gas under 5-8 atmospheres pressure. With the stirrer going, the mixture was saturated with acetylene at a given temperature (0-20°) and a given pressure (5-10 atm). after which either aldehyde or ketone was fed through the dropping funnel into the reactor at a uniform rate (over a period of 0.5-1 hour). The given pressure in the reactor (5-10 atm). was maintained during the entire experiment, readily maintained by regulating the feed rate of carbonyl compound and acetylene. Following addition of all aldehyde or ketone, the reaction mixture was stirred for another 30-40 minutes, treated with water (equal or double quantity according to the weight of alkali), the product neutralized with carbon dioxide, extracted with ether, dried with potash, and fractionated. After distilling off the ether, the acetylenic alcohol was first distilled in the usual manner, and then on a column with 25 theoretical plates. If necessary, the acetylenic alcohol after the first distillation, was again dried with potash.

Pressure greatly accelerated condensation of acetylene with aldehydes and ketones, and made it possible to effect this reaction within a short space of time (1-2 hours). There was also eliminated side formation of glycols, which increased considerably the yield of acetylenic alcohols, reaching almost theoretical values in the case of aliphatic and alicyclic ketones For condensation of ketones with acetylene, a pressure of 5 atm. was quite sufficient, while condensation of aldehydes with acetylene was carried out at 8-10 atmospheres of pressure. Better yields of acetylenic alcohols from condensation of ketones with acetylene were obtained at a temperature of 15-20°, and for condensation of aldehydes with acetylene, it was better to carry out reaction at a temperature of 0°, or even – 5°. Of real importance is good stirring of the reaction mixture, which becomes very viscous at the end of the experiment. In the reactor described, of 1 liter volume, stirring at 900-1000 r.p.m. was used, and for a reactor on larger scale (6 liters), stirring at 400-500 r. p. m. was found satisfactory. Ethers, acetals or hydrocarbons could be used as solvents for condensation of aldehydes and ketones.

Condensation of Acetylene with Acetaldehyde. a) A mixture of 65 g powdered potassium hydroxide and 250 ml of dry ether was saturated with acetylene at 0° and 10 atm. pressure. 28 g of acetaldehyde (b.p. 21-23°) was introduced into the reactor over a period of 50 minutes, with vigorous stirring; the mixture was stirred for another 20 minutes at 0° and 10 atm. pressure. The product was processed as described above and fractionated on a column. 9 g of 1-butyn-3-ol with b.p. 107-108° resulted: n_D^{20} 1.4250 [14]. Yield 20.2 %.

b) A mixture of 64 g of potassium hydroxide, 250 ml of ether (dry) and 3 ml of ethanol (95 %) was saturated with acetylene at 0° and 10 atm. pressure. 44 g of acetaldehyde (b.p. 21-22°) was introduced into the reactor over a period of 33 minutes, and the reaction mixture stirred for another 20 minutes, and treated in the usual fashion. 30 g of pure 1-butyn-3-ol with b.p. 107-108° resulted; n_D^{20} 1.4250. Yield was 43 %.

Condensation of Acetylene with Propionic Aldehyde. a) A mixture of 60 g of powdered potassium hydroxide and 300 ml of ether was saturated with acetylene at 0°, and a pressure of 8 atm. 29 g of propionic aldehyde (b.p. 47-49°) was introduced into the reactor over a period of 90 minutes. Stirring at 0° and at a pressure of 8 atm. was continued for another 30 minutes. After processing, 15 g of pure 1-pentyn-3-ol, with b.p. 124° resulted; n_D^{20} 1.4332 [15]. Yield 36 %.

b) A mixture of 64 g potassium hydroxide, 250 ml of dry ether and 5 ml of ethanol (95 %) was saturated with acetylene at 0° and 8.8 atm. pressure. 58 g of propionic aldehyde (b.p. 47-49°) was introduced into the reactor with vigorous stirring over a period of 30 minutes. The reaction mixture was then stirred for another 20 minutes. 38 g of pure 1-pentyn 3-ol with b.p. 124° resulted; n_D^{20} 1.4332. Yield 45.2 %.

Condensation of Acetylene with n-Butyric Aldehyde. 50 g of powdered potassium hydroxide and 250 ml of ether were saturated with acetylene at 0° and 10 atm. pressure. Within a period of 60 minutes, 32 g of n-butyric aldehyde (b.p. 74-76°) was introduced into the same apparatus. After stirring for another half-hour, followed by the usual treatment of product, 22 g of pure 1-hexyn-3-ol with b.p. 143.5°, resulted; n_D^{20} 1.4350 [15]. Yield was 51.5 %.

Condensation of Acetylene with Isobutyric Aldehyde. 80 g of powdered potassium hydroxide and 350 ml of ether were saturated with acetylene at 0° and a pressure of 8.6 atmospheres. 53 g of isobutyric aldehyde (b.p. 63-64°) was introduced into the reactor over a period of 70 minutes. 33 g of 4-methyl-1-pentyn-3-ol with b.p. 133° resulted; n_D^{20} 1.4353 [16]. Yield was 47.5 %.

Condensation of Acetylene with Hydrocinnamic Aldehyde. a) 40 g of the hydrocinnamic aldehyde was added to a mixture of 50 g of powdered potassium hydroxide and 250 ml of ether saturated with acetylene at 0° and a pressure of 8.4 atm.; over a period of 85 mintues, stirring then continued for another 30 minutes. After the usual treatment and distillation in vacuo, 18.5 g of pure 5-phenyl-1-pentyn-3-ol with b.p. 125-125.7° at 10 mm was isolated; n_D^{20} 1.5350. Yield 37.7 %.

b) 40 g of hydrocinnamic aldehyde was added over a period of 55 minutes to a mixture of 50 g of potassium hydroxide, 250 ml of dry ether, and 1.5 ml of ethanol (95%) saturated with acetylene at 0° and a pressure of 8.5 atm. After 30 minutes stirring, the product was treated as usual and fractionated in vacuo. 26 g of pure 5-phenyl-1-pentyn-3-ol with b.p. 125-126° at 10 mm was isolated; n_D^{20} 1.5350. Yield was 54.5%.

Condensation of Acetylene with Isovaleric Aldehyde. 48 g of powdered potassium hydroxide and 250 ml of ether were saturated with acetylene at 0° and 10 atm. pressure. 32 g of isovaleric aldehyde (b.p. 90-92°) was introduced into the apparatus over a period of 75 minutes. Stirring was continued for another 25 minutes. After the usual processing, followed by fractionation on a column, 31 g of 5-methy-1-hexyn-3-ol with b.p. 154-154.4°, resulted; n_D^{20} 1.4378. Yield was 74.5%.

Condensation of Acetylene with Enanthol. A mixture of 30 g powdered potassium hydroxide and 200 ml of ether was saturated with acetylene at 0° and 8 atm. pressure. 23 g of enanthol was introduced into the reactor over a period of 1 hour. Stirring was continued for another 30 minutes. 14.5 g of 1-nonyn-3-ol with b.p. 89-91° at 12 mm was isolated: n_D^{20} 1.4444 [17].

Condensation of Acetylene with Acetone. 60 g of powdered potassium hydroxide and 180 ml of ether were saturated with acetylene at 0° and 7 atm. pressure. 29 g of acetone was introduced into the receiver over a period of 30 minutes. Stirring was continued for another 30 minutes. After the usual treatment and fractionation on a column, 39 g of dimethylethynylcarbinol resulted with b.p. 103.5°; n_D^{20} 1.4211. Yield was 93%.

Condensation of Acetylene with Methylethyl ketone. A mixture of 65 g of powdered potassium hydroxide and 250 ml of ether was saturated with acetylene at 20° and 7 atm. pressure. 36 g of methylethyl ketone (b.p. 76 - 78°) was introduced into the reactor over a period of 45 minutes. Stirring was continued for another 30 minutes. After the usual treatment, and fractionation on a column, 39.2 g of 3-methyl-1-pentyn-3-ol with b.p. 121.5° was isolated; n_D^{20} 1.4309 [18, 19].

Condensation of Acetylene with Diethyl ketone. 42 g of powdered potassium hydroxide and 250 ml of ether at 0° and 7.6 atm. were saturated with acetylene. 30 g of diethyl ketone was introduced into the reaction mixture over a period of 100 minutes. After treatment and distillation on a column, 32 g of 3-ethyl-1-pentyn-3-ol with b.p. 137-138.4° was isolated. n_D^{20} 1.4364 [20, 21]. Yield was 92%.

Condensation of Acetylene with Di-n-propyl Ketone. 31 g of powdered potassium hydroxide and 50 ml of ether were saturated with acetylene at 0° and 7.2 atm. pressure. 29 g of di-n-propyl ketone was introduced into the reactor over a period of 80 minutes. Stirring was continued for another 30 minutes. After usual treatment and distillation on the column, 26 g of 3-propyl-1-hexyn-3-ol with b.p. 173-174° was isolated; n_D^{20} 1.4375 [22].

Condensation of Acetylene with Isobutyrone. 65 g of powdered potassium hydroxide, 250 ml of ether and 5 ml of ethanol (95%) were saturated with acetylene at 0° and 7.6 atmospheres pressure. 114 g of isobutyrone (b.p. 120 - 124°) was introduced into the reactor over a period of 40 minutes. Stirring was continued for another 15 minutes. After the usual treatment and fractionation on a column, 91 g of 4-methyl-3-isopropyl-1-pentyn-3-ol with b.p. 165.5° was isolated; n_D^{20} 1.4500 [21]. Yield was 65%.

Condensation of Acetylene with Cyclopentanone. 42 g of powdered potassium hydroxide, 200 ml of ether, and 3 ml of ethanol were saturated with acetylene at 0° and 8 atm. pressure. 52 g of cyclopentanone was introduced into the receiver over a period of 20 minutes. Stirring after introduction of the ketone was continued for another 15 minutes. After the usual treatment and fractionation on a column, 28 g of 1-ethynyl-1-cyclopentanol with b.p. 157° was isolated, m.p. 27° [23].

Condensation of Acetylene with Cyclohexanone. A mixture of 40 g of powdered potassium hydroxide and 250 ml of ether was saturated with acetylene at 0° and 7.6 atm. pressure. 29 g of cyclohexanone (b.p. 155°) was introduced into the receiver over a period of 75 minutes. Stirring was continued for another 30 minutes. After the usual treatment, 35.5 g of 1-ethynyl-1-cyclohexanol with b.p. 179° was isolated; m.p. 31-32° (from petroleum ether) [22, 23, 24]. Yield was 96.7%.

Condensation of Acetylene with Acetophenone. 65 g of powdered potassium hydroxide 250 ml of ether and 5 ml of ethanol were saturated with acetylene at 0° and 10 atm. pressure. 120 g of acetophenone was added to the reactor over a period of 45 minutes. After the usual treatment, 100 g of acetophenone was recovered and 17 g of 3-phenyl-1-butyn-3-ol, b.p. 82-83° at 4 mm; m.p. 49° [24, 25]. Yield was 11.6%, calculating on the basis of acetophenone taken for reaction, and on the basis of acetophenone reacted was 70%.

Condensation of Acetylene with Mesityl Oxide. 33 g of powdered potassium hydroxide, 250 ml of ether and 2.5 ml of ethanol were saturated with acetylene at 0° and 10 atm. pressure. 50 g of mesityl oxide was introduced into the reactor over a period of 35 minutes. Stirring was continued for another 30 minutes. After the usual treatment, 23 g of mesityl oxide was isolated and 2 g of pure 3,5-dimethyl-4-hexen-1-yn-3-ol with b.p. 65-66° at 17 mm; n_D^{20} 1.4629. The yield was 2.5% calculating on the basis of ketone introduced into reaction, and 5.2% on the basis of ketone reacted.

SUMMARY

A new method for condensing aldehydes and ketones with acetylene under pressure has been developed, which permits rapid synthesis of secondary and tertiary acetylenic alcohols in good yield.

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Condensation of [illegible] with [illegible]. [illegible] g of [illegible] were [illegible] with [illegible] the [illegible] period of 30 minutes [illegible] 23 g of [illegible] oxide [illegible] and 1 g of [illegible] n_D^{20} 1.4620. The yield was [illegible] in the [illegible] of [illegible] reacted.

SUMMARY

A new method for [illegible] which permits rapid synthesis of [illegible]

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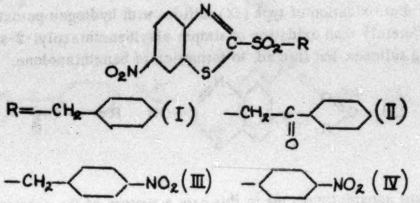
HYDROLYTIC RUPTURE OF BENZTHIAZOLYL-2-ARYL- AND ALKYLSULFONES

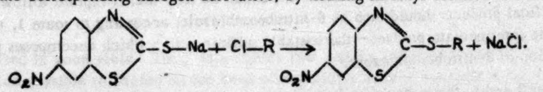
1. REACTION MECHANISM FOR RUPTURE OF 6-NITRO-BENZTHIAZOLYL-2-ARYL- AND ALKYLSULFONES

I. Ya. Postovsky and I. A. Alekseeva

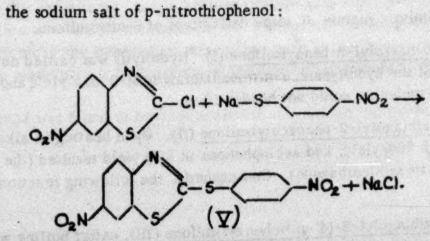
In studying certain benzthiazole (I - IV, VIII) sulfones, their instability relative to dilute acids and alkalies was observed. Under the influence of these substances, sulfones of the benzthiazole series undergo hydrolytic rupture, from which reaction products 6-nitro-2-benzthiazolone readily separates. This characteristic case of hydrolytic rupture of the sulfones is of decided theoretical interest, a fact which prompted the authors to engage in the task of clarifying the mechanism of this new type of rupture.



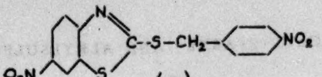
Sulfones result from oxidation of sulfides by potassium permanganate or hydrogen peroxide in acetic acid solution. The sulfides required for this purpose were synthesized by condensing the sodium salt of 2-mercapto-6-nitrobenzthiazole with the corresponding halogen derivative, by heating in ethyl alcohol with KI addition:

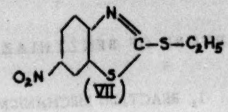


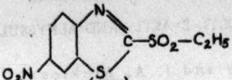
Synthesis of p-nitrophenylsulfide (V) was not accomplished in similar fashion because of the relatively low reactivity of the halogen in the p-nitrochlorobenzene. Sulfide (V) resulted in good yield on condensing 2-chloro-6-nitrobenzthiazole with the sodium salt of p-nitrothiophenol:



In approaching a study of the mechanism of rupture of sulfones in the benzthiazole series, it was necessary to clarify first of all whether or not hydrolytic rupture is characteristic only for sulfones, or whether similar corresponding sulfides of the benzthiazole series are not also subject to similar rupture. It was found that sulfides are not capable of hydrolytic rupture under those conditions wherein the sulfones rupture with relative facility upon reaction with aqueous solutions of acids and alkalies. This fact was established by studying the hydrolysis reaction of compound (III), and the corresponding initial sulfide (VI), as well as compounds (VII) and (VIII) with aliphatic radicals:

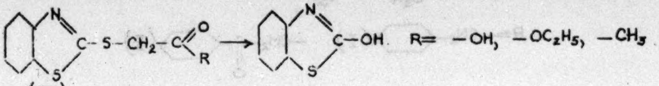

(VI)


(VII)


(VIII)

Thus, for example, sulfide (VI) did not change noticeably with 2 hours heating in 2N NaOH at 94°. However, under these conditions, the corresponding sulfone (III) was ruptured about 85%. Sulfide (VII) was hardly ruptured either by 1 hour heating with 2N NaOH at 94°, or by 1 hour heating with dilute hydrochloric acid at the same temperature, while at the same time sulfone (VIII) hydrolyzed smoothly under these conditions.

Hydrolytic rupture of sulfones of the benzthiazole series has not been described in the literature up to date. Only V. F. Kucherov [1] reported that oxidation of type (IX) sulfides with hydrogen peroxide at 60 - 70° in glacial acetic acid medium proceeds differently than oxidation of simple alkylbenzthiazolyl-2-sulfides, and does not lead to production of the corresponding sulfones, but instead, to formation of benzthiazolone:



(IX)

In the authors' opinion there apparently occurs in this case a rupture of the corresponding sulfone by oxidation, and not rupture of the C—S bond of the sulfide or sulfoxide.

The rupture of sulfones is thought to be possible according to one of four routes, as the result of an attack by the hydrolyzing agent (water) on two sides of the sulfo bonds (at the $C-SO_2$ and at the SO_2-R bonds), (see scheme).

From the given schemes for possible rupture reactions, it can be seen that if rupture follows along the lines of 1 or 2, that one of the final products should then be 6-nitrobenzthiazole; according to route 1, it forms directly, and according to 2, via the intermediate product — the unstable sulfinic acid — which decomposes with sulfur dioxide evolution and production of 6-nitrobenzthiazole.*

According to routes 3 and 4, there should be formed upon hydrolysis the 6-nitro-2-hydroxybenzthiazole (6-nitrobenzthiazolone-2), whereas by route 4, it would result via the stage of the corresponding sulfo acid, which, when boiled, decomposes, forming 6-nitrobenzthiazolone-2.**

Below are results of the hydrolytic rupture of some derivatives of 6-nitrosulfone.

1) Hydrolysis of 6-nitrobenzthiazolyl-2-benzylsulfone (I). Hydrolysis was carried out by heating the product in 2N NaOH. Upon acidification of the hydrolyzate, 6-nitrobenzthiazolone-2 in a yield about 90% theory was isolated; the other part of the ruptured molecule could not be identified.

2) Hydrolysis of 6-nitrobenzthiazolyl-2-phenacetylsulfone (II). Upon heating in alkaline as well as acid medium, 6-nitrobenzthiazolone-2 in 96% yield, and acetophenone in 60% yield resulted (the latter being isolated from the hydrolyzate in the form of its semicarbazone). Consequently, the following reaction took place: [see (A) on next page].

3) Hydrolysis of 6-nitrobenzthiazolyl-2-(4'-nitrobenzyl)sulfone (III). After boiling with 2N NaOH, 6-nitrobenzthiazolone-2 in 85% yield and p-nitrotoluene in approximately 52% yield of theory, were isolated and identified. Consequently, the hydrolysis in this case proceeded according to the scheme: [see (B) on next page].

In none of the given cases was it possible to isolate 6-nitrobenzthiazole, but each time the 6-nitrobenz-

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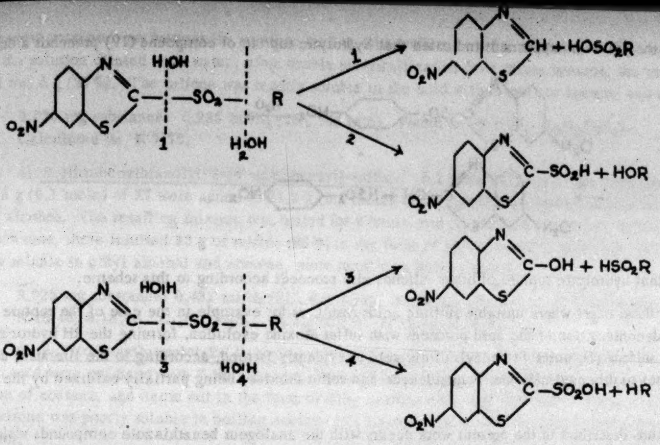
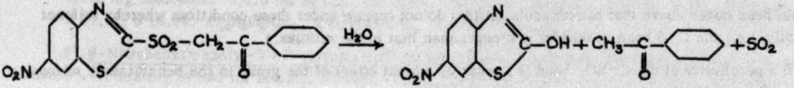
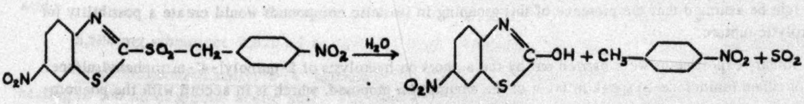
* Compare a similar reaction for benzthiazole-2-sulfinic acid [2].

** See rupture reaction for benzthiazol-2-sulfo acid [3].





(A)

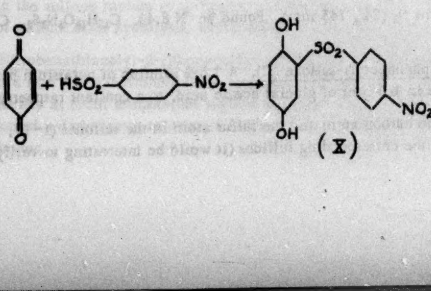


(B)

thiazolone-2 resulted in good yield. These data signify that rupture proceeds along routes 3 or 4. As yet, however, it has not been possible to decide on the basis of experimental data between 3 and 4, since the SO_2 could have been split off either from the benzthiazole sulfo acid or from the sulfinic acid, $R-SO_2H$.

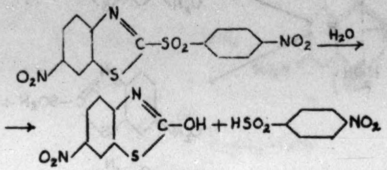
4) In the case of 6-nitrobenzthiazolyl-2-(4'-nitrophenyl)-sulfone (IV) hydrolysis it was possible to clarify the problem. In this experiment, p-nitrobenzenesulfinic acid was also isolated from the hydrolyzate of this experiment in addition to 6-nitrobenzthiazolone-2. The former is known to be a relatively stable compound. In fact, it was possible to prove the presence of this sulfinic acid in the mother liquor from the benzthiazolone, by adding p-quinone [4], whereupon 2,5-dihydroxy-4'-nitrodiphenylsulfone (X) resulted: [see (C) below).

This new compound was found to be identical with the sulfone synthesized from p-quinone and p-nitrobenzenesulfinic acid.



(X)

The results of the previous experiment indicated that hydrolytic rupture of compound (IV) proceeds along route 3.



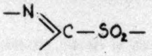
It is believed that hydrolytic rupture of other sulfones also proceeds according to this scheme.

Apparently, in those cases where unstable sulfinic acids result, as for example in the case of the rupture of sulfones (II) and (III), decomposition of the acid proceeds with sulfur dioxide evolution, forming the RH hydrocarbon. Upon hydrolysis of the sulfone (I), unstable benzylsulfinic acid is evidently formed; according to the literature data [5], the acid decomposes to dibenzylsulfoxide, benzaldehyde and sulfur dioxide, being partially oxidized by the air to benzylsulfo acid.

Hydrolytic rupture described in the present work occurs with the analogous benzthiazole compounds which do not contain the nitro group.

It has been stated above that benzthiazole sulfides do not rupture under those conditions whereby sulfones rupture readily, i.e., the C−S bond in sulfides is stronger than that in the sulfones.*

Such a peculiarity of the C−SO_2 bond is a result of mutual effect of the group in the benzthiazole sulfone molecule which has a characteristic sulfoazo methine grouping.



It might be assumed that the presence of this grouping in isosteric compounds would create a possibility for similar hydrolytic rupture.

Preliminary experiments were carried out by the authors on hydrolysis of 2-quinolyl-4'-nitrophenylsulfone. The results obtained (quinolone-2) speak in favor of the assumption proposed, which is in accord with the phenomenon discovered.

EXPERIMENTAL

I. Synthesis of Sulfides and Sulfones

1) 6-Nitrobenzthiazolyl-2-(benzyl)-sulfide: yellow needles, m.p. 114° (from alcohol), 114° indicated in the literature [6].

6-Nitrobenzthiazolyl-2-(benzyl)-sulfone (I), slightly-yellow needles with m.p. 192° (194° in the literature) [6].

2) 6-Nitrobenzthiazolyl-2-phenacetylsulfide. 21.2 g (0.1 mole) of 6-nitro-2-mercaptobenzthiazole was dissolved in a mixture of 200 ml. ethyl alcohol and 50 ml. of 2N NaOH. An alcoholic solution of 11.7 g (0.1 mole) of chloroacetophenone (m.p. 58 - 59°) was added to the hot solution of the sodium salt of potassium iodide, 16 g (0.1 mole). A yellow substance precipitated immediately. The reaction mass was boiled for 1 hour, poured into ice water, and the yellow needle precipitate filtered off. After double recrystallization from dilute alcohol, yellow needles with a constant m.p. of 129-130°, precipitated. Yield was 21 g (60%). The sulfide was readily soluble in methyl, ethyl and butyl alcohols, by heating, poorly so in benzene, and glacial acetic acid.

3.595 mg substance: 0.270 ml N_2 (24°, 745 mm). Found %: N 8.45. $C_{15}H_{10}O_3N_2S_2$. Calculated %: N 8.48.

3) 6-Nitrobenzthiazolyl-2-(phenacetyl)-sulfone (II). A 7.5% solution of potassium permanganate was added to a solution of 21 g of sulfide in 1.0 liter of glacial acetic acid, to a constant raspberry red coloration,

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* Evidently the distance between the carbon atom and the sulfur atom in the sulfones (I−IV, VIII) is greater than the distance between these atoms in the corresponding sulfides (it would be interesting to verify this assumption by X-ray analysis).

The excess potassium permanganate was then tied up with sodium bisulfite solution. Sulfone needles precipitated out from the solution diluted with water; after double recrystallization from dilute acetone, the m.p. was 173-174°. Yield was 5 g (25%). The sulfone was readily soluble in the cold with respect to acetone and in hot butyl alcohol.

3.270 mg substance: 0.235 ml N_2 (25°, 745 mm). Found %: N 8.07. $C_{15}H_{10}O_5N_2S_2$. Calculated %: N 7.73.

4) 6-Nitrobenzthiazolyl-2-(4'-nitrobenzyl)-sulfide. 0.1 mole (17.2 g) of p-nitrobenzyl chloride (m.p. 71°) and 16 g (0.1 mole) of KI were added to 21.2 g (0.1 mole) of 6-nitro-2-mercaptobenzthiazole in solution with 200 ml of alcohol. The resulting mixture was boiled for 2 hours, and poured into ice water. After recrystallization from nitrobenzene, there resulted 30 g of sulfide (88%) in the form of yellow needles with m.p. 181°. The sulfide was poorly soluble in ethyl alcohol and acetone, more readily in butyl alcohol.

3.925 mg substance: 0.431 ml N_2 (21°, 743 mm). 28.55 mg substance: 37.5 mg $BaSO_4$. Found %: N 12.46; S 18.04. $C_{14}H_9O_4N_3S_2$. Calculated %: N 12.12; S 18.46.

5) 6-Nitrobenzthiazolyl-2-(4'-nitrobenzyl)sulfone (III). 7 g (0.02 mole) of sulfide and 750 ml of glacial acetic acid were oxidized with 7.5% potassium permanganate. The reaction product was recrystallized from a large volume of acetone, and came out in the form of silky needles with m.p. 227-228°. Yield of sulfone was 6.5 g (85%). The sulfone was poorly soluble in boiling acetone and alcohol, but readily soluble in hot nitrobenzene, and insoluble in water.

4.075 mg substance: 0.416 ml N_2 (21°, 741 mm). 32.70 mg substance: 39.6 mg $BaSO_4$. Found %: N 11.57; S 16.60. $C_{14}H_9O_6N_3S_2$. Calculated %: N 11.07; S 16.90.

6) 6-Nitrobenzthiazolyl-2-(4'-nitrophenyl)-sulfide. 9 g of 2-chloro-6-nitrobenzthiazole (0.042 mole) was dissolved with heating in 500 ml of ethyl alcohol. 3.2 g NaOH was added to a hot solution of the sodium salt of p-nitrothiophenol (9 g of thiophenol in an alcoholic solution). A yellow-gray substance precipitated. The yield was 10.4 g (80%).

9.5 g of sulfide resulted as yellowish needles with m.p. 174-175° upon recrystallization from glacial acetic acid.

5.800 mg substance: 0.622 ml N_2 (19°, 749 mm). Found %: N 12.35. $C_{13}H_7O_4N_3S_2$. Calculated %: N 12.61.

7) 6-Nitrobenzthiazolyl-2-(4'-nitrophenyl)-sulfone (IV). 10.5 g (0.03 mole) of the sulfide was dissolved with heating in 500 ml of glacial acetic acid. The cooled sulfide acetate solution was oxidized with 7.5% permanganate solution. The resulting sulfone was recrystallized from a large volume of boiling acetone. Colorless, silky needles with m.p. 274-275°, yield 10.1 g, which amounted to about 84% of theory. The sulfone was poorly soluble in alcohol and acetone, glacial acetic acid and benzene.

4.700 mg substance: 0.460 ml N_2 (17°, 744 mm). Found %: N 11.27. $C_{13}H_7O_6N_3S_2$. Calculated %: N 11.50.

II. Hydrolytic Rupture of Sulfones.

1) Rupture of 6-Nitrobenzthiazolyl-2-(benzyl)-sulfone (I) a) Alkaline rupture. A suspension of 3.5 g (0.01 mole) of sulfone in 300 ml of 2N NaOH was heated in a round-bottomed flask equipped with reflux comdenser. A dark-brown solution gradually formed, with an odor of benzaldehyde. The alkaline solution was neutralized with dilute hydrochloric acid. The substance which precipitated was filtered off. The resulting product had an m.p. of 249-250°. A sample mixed with known 6-nitrobenzthiazolone-2 did not give depression in melting point. The yield of 6-nitrobenzthiazolone-2 was 2.1 g (91%).

b) Acid rupture. The acid rupture was carried out in a dilute hydrochloric acid medium (1:1). The acid hydrolyzate was made alkaline with concentrated alkali to a definite alkaline reaction. The results obtained were analogous to the results in the sulfone rupture experiments in alkaline medium. 3.6 g of 6-nitrobenzthiazolone-2 was isolated from 6.5 g of sulfone after hydrolysis, which amounted to 92% of theory.

2) Rupture of 6-Nitrobenzthiazolyl-2-(phenacetyl)-sulfone (II). a) Alkaline rupture. 0.1 g of sulfone (m.p. 173-174°) was placed in a round-bottomed flask equipped with reflux condenser. 5 ml of 2N—NaOH was poured into the flask. Already at room temperature rupture began, evident by gradual fading of the sulfone precipitate, and the formation of a dark-brown solution with strong acetophenone odor. The sulfone ruptured complated at 60° within 5 minutes.

The solution was extracted with ether. After distilling off the ether, there was a little liquid in the residue with strong acetophenone odor. Acetophenone was identified by its semicarbazone, obtained by addition of semicarbazide and sodium acetate to the liquid under investigation, with subsequent boiling of the mixture. The resulting product (0.03 g) had an m.p. of 199-200°. A sample mixed with known semicarbazone of acetophenone (m.p. 203°) did not give depression. The yield of acetophenone was approximately 60% of theory.

The alkaline solution was acidified with 50% acetic acid, whereupon 6-nitrobenzthiazolone-2 precipitated in the amount of 0.052 g (96%).

b) Acid rupture. Upon acid rupture, 6-nitrobenzthiazolone-2 and acetophenone (identified in the form of its semicarbazone) were isolated from the hydrolyzate.

3) Rupture of 6-Nitrobenzthiazolyl-2-(4'-nitrobenzyl)-sulfone (III). 6.4 g (0.02 mole) of sulfone (m.p. 181°) was heated with 2N NaOH (400 ml) in a round-bottomed flask equipped with reflux condenser. The precipitate dissolved gradually and the solution became dark-brown in color. Boiling was continued for approximately 2 hours. p-Nitrotoluene was distilled off from the alkaline solution with steam. The product isolated had an m.p. of 55°. A sample mixed with p-nitrotoluene melted without depression. Yield was 1.2 g (52%).

The alkaline solution which was filtered off was treated with 50% acetic acid to a weakly acid reaction to litmus. From this solution there precipitated a dark-yellow substance with m.p. 247-250°. The product, which was purified by recrystallization from alcohol with added activated charcoal, was in the form of colorless needles with m.p. 249-250°. The yield was 2.8 g (85%). The product was identified as 6-nitrobenzthiazolone by the melting point of a mixed sample.

4) Rupture of 6-Nitrobenzthiazolyl-2-(4'-nitrophenyl)-sulfone (IV). 0.2 g of sulfone was boiled for 0.5 hour with 40 ml of 2N NaOH in a flask equipped with reflux condenser. The solution gradually acquired a dark-brown color, and there settled to the bottom of the flask a precipitate of the sodium salt of 6-nitro-2-hydroxybenzthiazole. The precipitate was filtered off and dissolved in water. Upon acidification of the resulting solution with hydrochloric acid, there was formed a precipitate with m.p. 248-249°. There was no depression when melted with known 6-nitrobenzthiazolone-2. From the dark-brown filtrate of the sodium salt, the addition of dilute hydrochloric acid (1:1) precipitated out some more 6-nitrobenzthiazolone-2.

0.03 g of finely-powdered p-quinone was added to the hydrochloride filtrate. An amorphous precipitate formed upon gentle heating, which was filtered off. Recrystallized from dilute alcohol, the product had an m.p. of 208-209°. The resulting product had all the properties of 2,5-dihydroxy-4'-nitrodiphenylsulfone. A sample mixed with the known, synthesized for this purpose, 2,5-dihydroxy-4'-nitrodiphenylsulfone, did not give depression.

5) Synthesis of 2,5-Dihydroxy-4'-nitrodiphenylsulfone. 0.25 g of p-nitrobenzylsulfinic acid (prepared from p-nitrophenylsulfochloride by reduction with sodium sulfite [7]) was dissolved, with gentle heating, in 10 ml of water. The calculated quantity of powdered p-quinone (0.08 g) was added to the solution cooled to room temperature. Slightly yellow flakes immediately precipitated out at room temperature at the same time that the yellow crystalline precipitate of turbid quinone disappeared. The precipitate of resulting sulfone was filtered off and recrystallized from 30% alcohol. Needles with m.p. 210-211° resulted. The product was readily soluble at room temperature in alkali, forming a red-brown solution.

3.410 mg substance: 0.152 ml N_2 (25°, 738 mm). Found %: N 4.96. $C_{12}H_9O_6NS$.
Calculated %: N 4.72.

SUMMARY

1. It has been demonstrated that 6-nitrobenzthiazolyl-2-arylsulfones and alkylsulfones in alkaline and in acid solution are subject to hydrolytic rupture, with formation of 6-nitrobenzthiazolone-2.

2. The reaction mechanism for hydrolytic rupture of sulfones has been studied.

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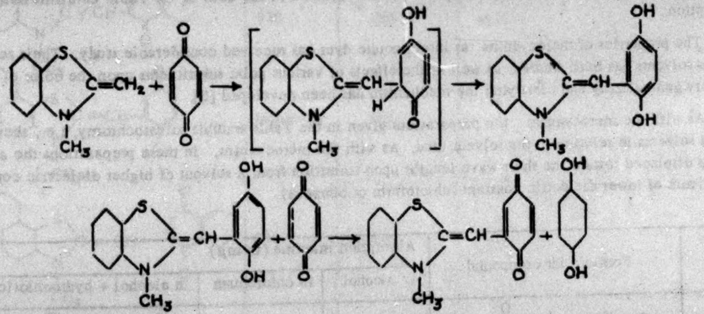
INTERACTION OF METHYLENE HETEROCYCLIC NITROGEN BASES WITH QUINONES

A. I. Kiprianov and A. V. Stetsenko

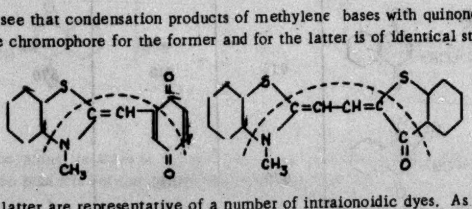
Several examples of condensation between quinones and methylene heterocyclic nitrogen bases are known. In 1937, the reaction of 2,3-dichloro-1,4-naphthoquinone with quinaldine iodomethylate in alkaline medium was described [1]. Somewhat later [2], a dark-colored product [Formula (I) in Table], with an absorption maximum in alcoholic solution of 620mμ, was isolated by autooxidation reaction of hydroquinone in an aqueous solution of borate buffer in the presence of the quaternary salt of 2-methylbenzthiazole. Gates [3], by mixing benzene solutions of 1,4-naphthoquinone and a methylene base obtained from the quaternary quinaldine salt, isolated a compound [formula (XIII) in Table] which was not studied further.

Reaction of methylene heterocyclic nitrogen bases with quinones is an individual case of the condensation of a compound containing an active methyl or methylene group. It has been known for a long time [4] that acetoacetic ester, malonic ester, acetylacetone and similar compounds, when interacted with quinones, in the presence of alkalies, give dark-blue condensation products. The mechanism of this reaction consists first in addition of a molecule of the compound with an active methylene group to the quinone molecule, with formation of the derivative of the corresponding hydroquinone, which is then oxidized by a second quinone molecule to the substituted quinone. For the interaction of N-methyl-2-methylenebenzthiazoline and p-quinone, this reaction can be represented by the following scheme:



The hydroquinone corresponding to the quinone used is always found to be a side product of the condensation. Sometimes it is possible to isolate it, and sometimes it participates in the formation of dark, slightly soluble precipitates which are found to be compounds of the quinhydrone type.

It is not difficult to see that condensation products of methylene bases with quinones are quite close to dyes of the merocyanin class. The chromophore for the former and for the latter is of identical structure:



The former and the latter are representative of a number of intraionoidic dyes. As with the merocyanins, the condensation products between quinones and methylene bases are found to be polymethine dyes; however, compared to the typical polymethine dyes, they have received but little study.

The authors arranged to synthesize a series of compounds of this type, condensing methylene bases of various nitrogen heterocycles with various quinones. A synthetic method for these characteristic compounds, as well as their absorption curves in various solvents, and some of their conversions, was studied.

The synthetic method was quite simple. A benzene solution of the methylene bases resulted from the quaternary salt of the base taken. Sometimes chloroform was used as the solvent. The base solution was mixed with the quinone solution in the same solvent. The mixture was left at room temperature for 45 - 60 minutes. The resulting blue or blue-black product was filtered off and purified. Substances were always taken for reaction in the ratio of 1 mole of methylene base to 2 moles of quinone. If 1 mole of quinone is taken, the yield is approximately doubled. Upon prolonged standing, the intensely-colored solution became yellow-green, and a poorly-soluble residue, dark in color, was formed.

Low yields of pure products resulted upon interaction of methylene bases with p-benzoquinone, apparently related to formation of poorly-soluble compounds of the quinhydrone type. Solutions of methylene bases obtained from quaternary salts of 2-methylthiazole, 2-methyloxazole, α-picoline and 2,3,3-trimethylindolenine, when reacted with quinones, became intensely blue, without formation of precipitate, and coloration disappeared, especially in light. Anthraquinone and phenanthraquinone, with methylene bases of heterocyclic nitrogen under the conditions indicated, did not produce any colored products.

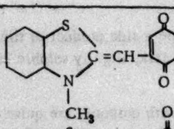
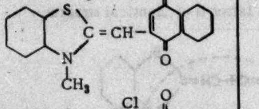
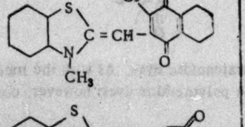
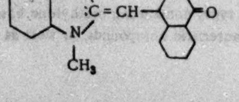
Formulas are given in the Table for compounds obtained by the authors, as well as their absorption maxima in alcohol, chloroform and alcohol containing added hydrochloric acid.

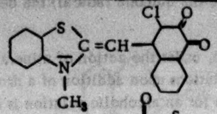
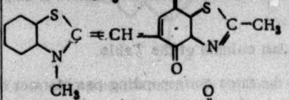
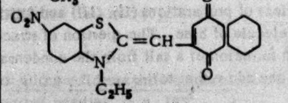
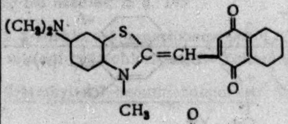
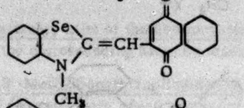
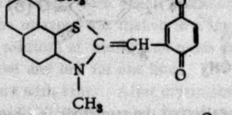
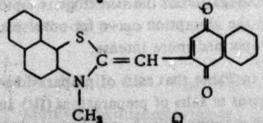
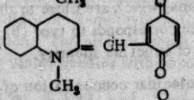
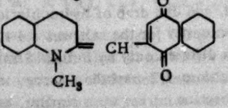
Absorption curves in alcohol and chloroform for the preparations given in the Table were broad, without sharp maxima. All preparations were deeply colored. Absorption maxima, as a rule, were about 600 mμ and higher. Deep coloration is a result of the quinoid ring present in the molecule. The corresponding merocyanins are less deeply colored.

Insofar as the condensation products of methylene bases with quinones are similar in structure to that of merocyanin it might be assumed that the rule established for relating color to structure for the merocyanins would also be accurate for the other compounds in question. Examination of the data in the Table confirms completely this assumption.

The properties of merocyanins as intraionoidic dyes has received considerable study. Their relation to various solvents has been studied, as well as the effects of various polar substituents upon the color of merocyanins. A theory generalizing and clarifying the mechanism has been developed [5].

As with the merocyanins the preparations given in the Table exhibit solvatochromy, i.e., they change color in neutral solvents in relation to the solvent used. As with the merocyanins, in these preparations the absorption maximum is displaced toward the short wave lengths upon transition from a solvent of higher dielectric constant (alcohol) to a solvent of lower dielectric constant (chloroform or benzene).

Number of compound	Formula for compound	Absorption maxima (in mμ)		
		In alcohol	in chloroform	In alcohol + hydrochloric acid
(I)		Insoluble	580	550
(II)		610	615	570
(III)		670	640	–
(IV)		640	620	430

Number of compounds	Formula for compound	Absorption maxima (in mμ)		
		In alcohol	In chloroform	In alcohol + HCl
(V)		650	645	420
(VI)		Insoluble	680	–
(VII)		Insoluble	560	–
(VIII)		680	660	620
(IX)		610	600	580
(X)		Insoluble	620	–
(XI)		640	630	580
(XII)		Insoluble	600	–
(XIII)		670	640	500

The rules established with merocyanins relative to the effect of polar substituents upon color, are also accurately reproducible for the condensation products between methylene bases and quinones.

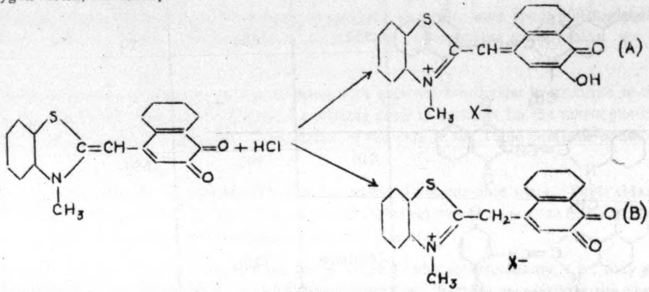
Introduction of a negative group into the benzene ring of the nitrogen heterocycle displaces the absorption maximum to the short wave lengths [transition from preparation (II) to preparation (VII)]. Introduction of a negative substituent into the quinone ring, on the other hand, gives displacement of the absorption maximum toward the long wave lengths (transition from (II) to (III) and from (IV) to (V)). The replacement of hydrogen atoms in the heterocyclic radical by a positive group invokes a strong intensification of the color [transition from (II) to (VIII)]. The replacement of a less basic heterocyclic radical by a more basic gives the same effect [transition from (I) to (XII) and from (II) to (XIII)].

All of these facts can be readily summarized by the following statement: the more polar their molecules (the more positive the nitrogen heterocyclic radical and the more negative the quinone radical) the deeper the color of condensation products between methylene bases and quinones.

The condensation products of methylene bases with quinones give, under the action of mineral acids, salts, which can be observed by a sharp color change in their alcoholic solutions upon addition of a drop of hydrochloric acid. In converting from base to salt, the absorption maximum for an alcoholic solution is displaced (without fail) toward the short wave lengths.

Absorption maxima for hydrochloride salts are given in the last column of the Table.

The authors isolated and analyzed in their individual states the three corresponding perchlorates obtained by addition of sodium perchlorate solution to hydrochloride salt solutions of preparations (II), (III) and (XIII). Analysis indicated that one molecule of acid was combined with one molecule of base. The question of structure for these salts was solved on grounds of spectroscopic observations. In formation of a salt from the condensation product between methylene base and quinone, the proton of the acid can add either to the methine group, or to one of the oxygen atoms, for example:



It is not difficult to observe that salts of the (B) type, where conjugation of the two rings is ruptured, should be weakly colored, and that their absorption curve should be similar to the absorption curve for corresponding quinones. On the other hand, coloration for salts of type (A) should be deeper and more intense.

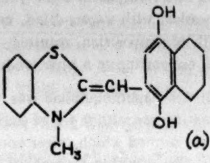
It can be seen from the absorption maxima of the salts given in Table that salts of preparations I, II, VIII, IX, XI and XIII have structures corresponding to type (A). With regard to salts of preparations (IV) and (V), then, judging from the yellow color of their solutions, and by their absorption maxima, which are close to the absorption maxima for the corresonding quinones, it might be assumed that their structure corresponds to type (B). By measuring the absorption intensity for these two salts, it is possible to solve the question of structure identity.

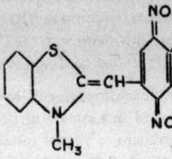
The absorption curves for alcoholic solutions of one and the same molecular concentration of preparation (IV), and its corresponding quinone (1,2-naphthoquinone) were measured, and one drop of hydrochloric acid was added to a solution of preparation (IV). It was found that the absorption intensity for the salt was 4.4 times greater than the intensity for quinone absorption, although the absorption maxima differed only by 5 mμ. Similar measurements were carried out with salt solutions of preparation (V) and of 3-chloro-1,2-naphthoquinone, where it was found that in this case absorption intensities are almost identical, the absorption curves were similar, and the maxima differ by only 7 mμ. It follows from these data that preparation (IV) gives with hydrochloric acid a salt corresponding to type (A), and preparation (V) corresponding to type (B). Such difference in relationship between preparations (IV) and (V) with regard to acid is apparently explicable by the fact that preparation (V), under the influence of a chlorine atom, possesses depressed basic properties for the quinone ring.

The condensation products of methylene bases with quinones are readily reduced with decolorization, converting to the corresponding hydroquinone derivative. Reduction can be effected with sodium bisulfite in alkaline solution. The resulting colorless or light-yellow solution possessed the properties of Cuba wood. Tissue paper moistened with the solution became colored rapidly in the air, acquiring the color of the dye used in the reduction. Reduction can also be carried out with tin and hydrochloric acid.

The authors obtained the dihydroxyderivative (a) from product (II) upon its reduction by the first and second methods.

Its structure was proved by its conversion to diacetyl and dimethoxy derivatives.


(a)


(b)

From the same preparation (II) there was obtained, by heating it with hydroxylamine hydrochloride, a yellow crystalline dioxime (b).

EXPERIMENTAL

3-Chloro-1,2-naphthoquinone [6] was obtained by chlorination of 1,2-naphthoquinone in glacial acetic acid. Long red needles, m.p. 173°.

2,3-Dichloro-1,4-naphthoquinone [7] was prepared from α-naphtholsulfonic acid by treating it with Berthollet's salt and hydrochloric acid. Yellow needles with m.p. 193°.

2-Methyl-4,7-benzthiazolquinone. Synthesized according to Fried and Reitz [8]. Fine yellow needles, m.p. 159°.

Quaternary salts of the heterocyclic bases, containing an active methyl group in the α-position, were obtained from the corresponding bases by reacting with alkyl halides or dialkyl sulfates.

2-(3'-Methylbenzthiazolinylidene-2'-methyl)-1,4-benzoquinone (I). 0.27 g of potash in 2 ml of water and 10 ml of benzene were added to a solution of 0.27 g of methylmethosulfate 2-methylbenzthiazole in 2 ml of water. The mixture was shaken in a separatory funnel. After standing, the water layer was separated, and to the benzene solution of methylene bases there was added 0.21 g of 1,4-benzo quinone in 5 ml of benzene. The mixture was stirred and left for one hour. The colored product which precipitated was washed with water, boiling alcohol and then with ether. After crystallization from chloroform or benzene, violet crystals with metallic luster resulted, m.p. 237° (in this case, and others to follow, uncorrected melting points are given). Yield was 0.03 g (14%). The product was poorly soluble in alcohol and ether, better in chloroform and benzene, and insoluble in water.

Found %: N 5.13, 5.08. $C_{15}H_{11}O_2NS$. Calculated %: N 5.20.

2-(3'-Methylbenzthiazolinylidene-2'-methyl)-1,4-naphthoquinone (II) was synthesized from 1 g of methylmethosulfate of 2-methylbenzthiazole, 1.35 g of potash and 1.15 g of 1,4-naphthoquinone, as in the preceding preparation. The product which precipitated out was washed with boiling alcohol and recrystallized from benzene. Long violet needles with copper luster, m.p. 247°, with decomposition. Yield was 1.02 g (88.3%).

Found %: N 4.19, 4.24. $C_{19}H_{13}O_2NS$. Calculated %: N 4.39.

To obtain the perchlorate, 0.2 g of resulting product was dissolved in benzene, and 3 drops of concentrated hydrochloric acid plus 3 ml of water added to the solution. After vigorous stirring, the water layer was separated, filtered, and an aqueous solution of sodium perchlorate added to it. The resulting red, amorphous precipitate was filtered off, dried and crystallized from absolute alcohol, m.p. 230°. Yield was 0.17 g (65%). The product hydrolyzed very readily with water and pure alcohol.

Found %: N 3.50, 3.52. $C_{19}H_{13}O_2NS \cdot HClO_4$. Calculated %: N 3.33

In order to obtain the 2-(3'-methylbenzthiazolinylidene-2'-methyl)-1,4-naphthoquinone dioxime, a mixture of 0.2 g of this preparation and 0.2 g of hydroxylamine hydrochloride were heated on a water bath for 2 hours with 1.5 ml of pyridine and 1.5 ml of absolute alcohol. The blue solution became yellow. It was evaporated to dryness, and 3 ml of water added to the residue. The part which did not dissolve in water was filtered and recrystallized from dilute alcohol. Orange-yellow, finely crystalline powder, m.p. 73°. Yield was 0.07 g (33%).

Found %: N 11.92, 11.95. $C_{19}H_{15}O_2N_3S$. Calculated %: N 12.03.

2-(3'-Methylbenzthiazolinylidene-2'-methyl)-1,4-naphthohydroquinone. a) 0.4 g of 2-(3'-methylbenzthiazolinylidene-2'-methyl)-1,4-naphthoquinone in 10 ml of alcohol was heated with 4 ml of concentrated hydrochloric acid and 0.4 g of stannous chloride, to the formation of a transparent light-yellow solution. After cooling, a crystalline precipitate separated, which was filtered, washed with water, dried, and recrystallized from dilute alcohol. Large colorless crystals, with m.p. 167°, with decomposition, resulted. Yield was 0.32 g (80%). The alkaline solution of the preparation oxidized readily, converting to a blue product.

b) 0.2 g of 2-(3'-methylbenzthiazolinylidine-2-methyl)-1,4-naphthoquinone was mixed with 0.4 g of caustic soda in 20 ml of water, and treated in a stream of illuminating gas with 0.4 g of sodium bisulfite and gentle heating and stirring. After 30 minutes, a yellow solution was formed which, after cooling, was neutralized with dilute hydrochloric acid by use of Congo red indicator. The resulting amorphous precipitate was filtered off, dried and crystallized from dilute alcohol. Colorless, crystalline powder, m.p. 167°, with decomposition. Yield was 0.13 g (65%).

To obtain the diacetyl derivative, 0.2 g of this hydroquinone was heated with 1 ml of acetic anhydride on a boiling water bath for 2 hours After cooling, 3 ml of water was added to the mixture. The resulting product was filtered off, washed with water, and dried. After crystallization from 50% alcohol, colorless crystals with m.p. 144°. Yield was 0.2 g (83%).

Found %: N 3.54, 3.58. $C_{22}H_{19}O_4NS$; Calculated %: N 3.47.

Dimethyl Ester of 2-(3'-methylbenzthiazolinylidene-2'-methyl)-1,4-naphthohydroquinone. An alkaline solution of 2-(3'-methylbenzthiazolinylidene-2'-methyl)-1,4-naphthohydroquinone in an atmosphere of illuminating gas was treated with dimethyl sulfate excess. The resulting voluminous precipitate was filtered off and recrystallized from alcohol. A yellow crystalline product, m.p. 54°. Yield was 0.16 g (76%).

Found %: N 3.86, 3.87. $C_{21}H_{19}O_2NS$. Calculated %: N 4.01.

2-(3'-Methylbenzthiazolinylidene-2'-methyl)-3-chloro-1,4-naphthoquinone (III). 0.27 g of 2-methylbenzthiazol methylmethosulfate in 10 ml of water was shaken in a separatory funnel with 0.22 g of 2,3-dichloro-1,4-naphthoquinone [7] in 10 ml of chloroform and 0.27 g of potash in 5 ml of water. The aqueous layer was separated, and from the blue chloroform solution a precipitate separated after 1 hour which was filtered and recrystallized from chloroform. Blue crystals, m.p. 194°. Yield was 0.14 g. (41 %);

Found %: N 4.11, 4.13; Cl 10.03, 10.02. $C_{19}H_{12}O_2NSCl$. Calculated %: N 3.96, Cl 10.04.

The perchlorate was obtained from an alcoholic solution of the hydrochloride salt by reacting the solution with sodium perchlorate. 0.24 g (68%) of light-yellow crystalline powder with m.p. 203-204° was isolated from 0.3 g of the preparation after recrystallization from absolute alcohol.

Found %: N 2.90, 2.95; Cl 15.30, 15.27. $C_{19}H_{12}O_2NSCl \cdot HClO_4$. Calculated %: N 3.08; Cl 15.63.

4-(3'-Methylbenzthiazolinylidene-2'-methyl)-1,2-naphthoquinone (IV) was obtained from 0.27 g of 2-methylbenzthiazole methylmetho sulfate 0.27 g of potash and 0.31 g of 1,2-naphthoquinone as before. Fine blue crystals with m.p. 223°. Yield was 0.1 g. (32%).

Found %: N 4.10, 4.12. $C_{19}H_{13}O_2NS$. Calculated %: N 4.39.

4-(3'-Methylbenzthiazolinylidene-2'-methyl)-3-chloro-1,2-naphthoquinone (V) was obtained from 0.27 g of 2-methylbenzthiazole methyl methosulfate, 0.27 g of potash and 0.19 g of 3-chloro-1,2-naphthoquinone as with the preceding. After boiling with alcohol, the product was recrystallized from chloroform. Fine crystals, m.p. 151°. Yield was 0.08 g. (23%).

Found %: N 3.77, 3.75; Cl 9.87, 9.80. $C_{19}H_{12}NSCl$. Calculated %: N 3.96; Cl 10.04.

5-(3'-Methylbenzthiazolinylidene-2'-methyl)-2-methyl-4,7-benzthiazolquinone (VI). Obtained from 0.26 g of 2-methylbenzthiazole methyl methosulfate, 0.47 g of potash and 0.3 g of 2-methyl-4,7-benzthiazolquinone, as in the preceding. The condensation product was recrystallized from benzene. Blue needles with m.p. 234-235°. Yield was 0.16 g (50 %).

Found %: N 8.04, 8.10. $C_{17}H_{12}O_2N_2S_2$. Calculated %: N 8.23.

2-(3'-Ethyl-6'-nitrobenzthiazolinylidene-2'-methyl)-1,4-naphthoquinone (VII) was synthesized from 0.35 g of 2-methyl-6-nitrobenzthiazole iodoethylate, 0.31 g of 1,4-naphthoquinone and 0.27 g of potash. Red crystals with copper luster, m.p. 309°. Yield was 0.08 g (22%).

Found %: N 7.19, 7.22. $C_{20}H_{14}O_4N_2S$. Calculated %: N 7.40.

2-(3'-Methyl-6'-dimethylaminobenzthiazolinylidene-2'-methyl)-1,4-naphthoquinone (VIII) was synthesized from 0.33 g of iodomethylate of 2-methyl-6-dimethylaminobenzthiazole, 0.31 g of 1,4-naphthoquinone and 0.27 g of potash as with preceding. After boiling with alcohol, and crystallizing from benzene, green platelets with m.p. 216° resulted. Yield was 0.09 g (26%).

Found %: N 7.55, 7.50. $C_{21}H_{18}O_2N_2S$. Calculated %: N 7.73.

2-(3'-Methylbenzselenazolinylidene-2'-methyl)-1,4-naphthoquinone (IX) was obtained from 0.32 g of 2-methylbenzselenazole methylmethosulfate, 0.27 g of potash and 0.31 g of 1,4-naphthoquinone. Fine blue crystals with m.p. 172°, with decomposition. Yield was 0.13 g (36%).

Found %: N 3.65, 3.68. $C_{19}N_{13}O_2NSe$. Calculated %: N 3.82.

2-(3'-Methyl-6',7'-benzobenzthiazolinylidene-2'-methyl)-1,4-benzoquinone (X). Obtained from 0.64 g of 2-methyl-6,7-benzobenzthiazole methyl metho sulfate, 0.54 g of potash and 0.42 g of 1,4-benzoquinone. Violet, fine crystalline powder, m.p. 209°, with decomposition. Yield was 0.2 g. (32%).

Found %: N 4.48, 4.51. $C_{19}H_{13}O_2NS$. Calculated %: N 4.38.

2-(3'-Methyl-6',7'-benzobenzthiazolinylidene-2'-methyl)-1,4-naphthoquinone (XI), was obtained from 0.32 g of 2-methyl-6,7-benzobenzthiazole methyl methosulfate, 0.27 g of potash and 0.31 g of 1,4-naphthoquinone. Fine blue crystals with copper luster, m.p. 246°. Yield was 0.16 g (44%).

Found %: N 3.95, 4.00. $C_{23}H_{15}O_2NS$. Calculated %: N 3.79.

2-(1'-Methylquinolylidene-2'-methyl)-1,4-benzoquinone (XII) was obtained from 0.54 g of quinaldine methyl methosulfate, 0.24 g of sodium hydroxide and 0.42 g of 1,4-benzoquinone. Fine blue crystals, m.p. 169°, with decomposition. Yield was 0.09 g (17%).

Found %: N 5.14, 5.16. $C_{17}H_{13}O_2N$. Calculated %: N 5.32

2-(1'-Methylquinolylidene-2'-methyl)-1,4-naphthoquinone (XIII) was obtained from 1.08 g of quinaldine methylmethosulfate, 0.48 g of sodium hydroxide and 1.21 g of 1,4-naphthoquinone. Violet needles with golden luster, m.p. 178°. Yield was 0.31 g (26%).

Found %: N 4.60, 4.53. $C_{21}H_{15}O_2N$. Calculated %: N 4.47.

The perchlorate was obtained by addition of sodium perchlorate to a solution of the base in hydrochloric acid. After recrystallization from absolute alcohol, there resulted fine red crystals, m.p. 207°, with decomposition. Yield was 0.13 g (50%).

Found %: N 3.19, 3.17; Cl 8.54, 8.60. $C_{21}H_{15}O_2N \cdot HClO_4$. Calculated %: N 3.38; Cl 8.82.

SUMMARY

13 condensation products have been obtained by reacting methylene heterocyclic nitrogen bases with 1,4-benzoquinone, 1,2- and 1,4-naphthoquinones, and their chlorine substitution products, as well as with 2-methyl-4,7-benzthiazolquinone, representing intraionoidic dyes of the merocyanin type. The absorption maxima for these dyes in neutral and acid solutions have been determined.

Perchlorates and other derivatives have been obtained from some of the condensation products of methylene bases with quinone.

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PHENYLAMIDATION OF DIBASIC CARBOXYLIC ACIDS WITH DIPHENYLSULFAMIDE

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It was found recently that upon reacting a sulfamide with dibasic carboxylic acids, there is formed, depending upon the structure of the acid, either the diamide of the dicarboxylic acid, or the imide [1]. In this work the reaction of diphenylsulfamide with dicarboxylic acids was studied. It was found that the sulfamide reaction and the diphenylsulfamide reaction with dicarboxylic acids was not the same. Thus, reaction of sulfamide with oxalic acid resulted in evolution of carbon dioxide, but neither formamide nor formamidine (compare [2]), nor oxamic acid, nor oxamide separated [1]. Upon reacting diphenylsulfamide with oxalic acid, carbon dioxide was evolved, but along with rupture of oxalic acid there also proceeded phenylamidation, and the oxalic acid dianilide was formed, although in small yields (25%). Reacting sulfamide with dicarboxylic acids readily giving internal anhydrides (succinic, glutaric, phthalic) gave only cyclic imides (along with succinamic acid in the case of succinic acid) [1]. Diphenylsulfamide reacted with phthalic acid and with its anhydride to give the phenylamide, but with succinic and glutaric acids, it gave dianilides instead of phenylamides. It is of interest that malonic acid gave only acetamide with sulfamide – it was not possible to isolate malonamide. With diphenylsulfamide, malonic acid gave the dianilide of malonic acid only – acetanilide failing to separate. Thus, sulfamide caused rupture of malonic acid, and diphenylsulfamide reacted with the former without splitting off carbon dioxide. Sulfamide and diphenylsulfamide reacted analogously with diethylmalonic acid – carbon dioxide being split off in both cases, with formation of diethylacetic acid amide and anilide. Isophthalic acid reacted normally with diphenylsulfamide.

Thus, in the amidation of dibasic acids with sulfamides, the formation of cyclic imides (succinic, glutaric and phthalic acids) proceeded more rapidly, and carbon dioxide was split off more rapidly (oxalic and malonic acids). Dianilides were more readily formed upon phenylamidation (oxalic, succinic and glutaric acids) and carbon dioxide split out with greater difficulty. Formation of cyclic phenylimides upon phenylamidation took place only for acids which form anhydrides with exceptional ease (phthalic, but not succinic or glutaric).

Phenylamidation of dibasic carboxylic acids proceeds under mild conditions and in good yields (with the exception of oxalic acid), and can be readily carried out with very small amounts of substance, and therefore can be recommended for identification of dicarboxylic acids, taking into particular account the fact that dianilides of an impressive majority of dicarboxylic acids are poorly soluble, high melting and crystallize readily.

EXPERIMENTAL

Phenylamidation of Dibasic Acids with Diphenylsulfamide. A mixture of 0.005 mole of dicarboxylic acid and 0.01 mole of diphenylsulfamide (2.48 g) was heated with 5.0 ml of pyridine for 4 hours (in some cases 6 hours) on an oil bath at 115-120° (in some cases 100 or 80°). Pyridine was distilled off from a water bath in vacuo, the residue treated with 5.0 ml of 1N sodium hydroxide solution, the residue sucked dry by filtration and washed with water. For purification, the reaction product was recrystallized from a suitable solvent.

Thus there resulted:

1) From oxalic acid – the dianilide of oxalic acid, m.p. 245-246° after recrystallization from benzene (uncorrected); the yield was 14% of theory (reaction at 115-120° for 4 hours), 19.3% (at 80°, 10 hours), 25% (at 70°, 6-10 hours).

2) From malonic acid – the dianilide of malonic acid, m.p. 222-223° after recrystallization from alcohol (uncorrected); yield was from 73.2 to 75.5% of theory (reaction at 115-120°, 100 and 80°, 4 and 10 hours).

3) From diethylmalonic acid – the anilide of diethylacetic acid, m.p. 122-124° after recrystallization from carbon tetrachloride (uncorrected); yield 95.0% of theory.

4) From succinic acid – the dianilide of succinic acid, m.p. 226-228° uncorrected after recrystallization from alcohol; yield was 67.1 and 82.7% of theory (reaction at 115-120° and at 100°, 4 hours).

5) From glutaric acid – the dianilide of glutaric acid, m.p. 221-222° after recrystallization from alcohol (uncorrected); yield 86.0% of theory.

6) From adipic acid – adipic acid dianilide, m.p. 234-236° after recrystallization from alcohol (uncorrected); yield was 84.4% of theory.

7) From phthalic acid or from phthalic anhydride – phenylphthalimide, m.p. 202-203° (uncorrected) after recrystallization from alcohol; yield was 96.8% of theory.

8) From isophthalic acid – the dianilide of isophthalic acid, m.p. 275-276° from acetic acid after recrystallization; yield was 96.8% of theory.

All of the substances were identified according to the melting point for a mixed sample with known pure preparations.

According to the literature data, isophthalic acid dianilide melts at 250° [3]. For comparison, the dianilide of isophthalic acid was prepared from the dichloroanhydride of isophthalic acid and aniline excess in benzene solution. The preparation synthesized according to this method, like a sample mixed with the substance which was obtained by direct phenylamidation, melted at 275-276° (uncorrected). Thus the literature data [3] are inaccurate; in actuality, the dianilide of isophthalic acid melts at 275-276° (uncorrected).

Amidation of Diethylmalonic Acid with Sulfamide. Amidation of diethylmalonic acid was carried out in order to compare the reaction of sulfamide and of diphenylsulfamide with this acid. A mixture of 0.01 mole of diethylmalonic acid (1.61 g), 0.02 mole of sulfamide (1.92 g) and 5.0 ml of dry pyridine was heated on a boiling water bath for 3 hours. Pyridine was distilled off in vacuo, and to the residue was added 10 ml of a 2N solution of soda, and the water evaporated in vacuo at 40°. Diethylacetic acid amide was extracted from the dry residue by ether. Yield was 0.95 g, i.e., 82.5% of theory. After recrystallization from alcohol, m.p. was 105-106° (uncorrected), which corresponded to the literature data [4].

SUMMARY

1. The reaction of diphenylsulfamide with dicarboxylic acids has been studied.

2. It has been demonstrated that dianilides result in good yields from phenylamidation of oxalic, malonic, succinic, glutaric, adipic and isophthalic acids, using diphenylsulfamide.

3. Phthalic acid and its anhydride form phenylamide upon phenylamidation.

4. Diethylmalonic acid upon phenylamidation gives the anilide of diethylacetic acid.

5. Direct phenylamidation of a dicarboxylic acid can be used for purposes of identification with considerable success.

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* See Consultants Bureau Translation, p. 1191.

** See Consultants Bureau Translation, p. 1653.

SYNTHETIC INVESTIGATION IN THE INDOLE DERIVATIVE SERIES

III. SYNTHESIS OF 1,3-DIMETHYL-3-β-DIMETHYLAMINOETHYL-5-HYDROXYINDOLIN-2-ONE (DEHYDROESEROLINMETHINE) AND 1,3-DIMETHYL-3-γ-DIMETHYLAMINOPROPYL-5-HYDROXYINDOLIN-2-ONE (DEHYDROHOMOESEROLINMETHINE) URETHANES

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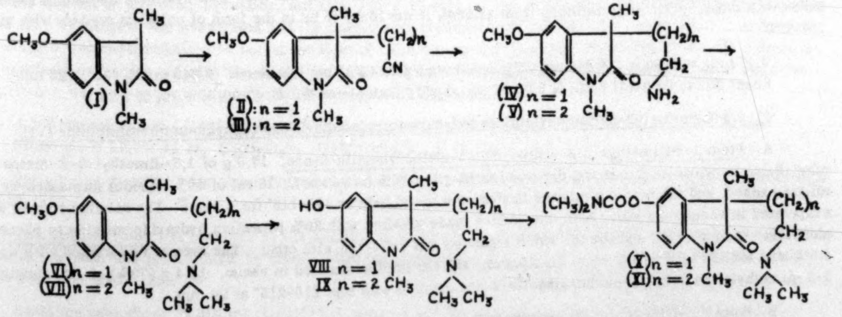
The simplest eserine-like substances known up to the present time could be divided perhaps into two large groups, depending upon the nature of the base of which they are derivatives. The first group is composed of weakly basic eserine analogs, in which the amino group is tied up with the aromatic ring – carbamine esters of substituted aniline, indolines, pyridines, quinolines, and so forth. To the second group could belong urethanes of phenols which possess an amino group in the side chain, and which are related to those stronger bases – the myotine-type substances. For all compounds of the first group there is the characteristic shortcoming that their salts, with the exception of some quaternary salts, hydrolyze readily in aqueous solution, due to which fact rapid inactivation of the preparations occurs. Compounds of the second group are far-removed from eserine in their structure, and are not in the full sense of this word, analogs of the alkaloid.

With consideration for the above state of affairs, the authors decided to investigate urethanes of the 5-hydroxyindoline series, which possess an amino group in the side chain, and which at the same time are found to be derivatives of p-aminophenol which approximate eserine structurally. As such, the first group selected was the dimethylurethanes of 1,3-dimethyl-3-β-dimethylaminoethyl-5-hydroxyindolin-2-one (dehydroeserolinmethine) (X) and 1,3-dimethyl-3-γ-dimethylaminopropyl-5-hydroxyindolin-2-one (dehydrohomoeserolinmethine) (XI), synthesis of which is described in the present article.



1,3-Dimethyl-5-methoxyindolin-2-one (I) was condensed with chloroacetonitrile [1], the condensation product (II) hydrogenated over skeletal nickel catalyst in the presence of ammonia, and the primary amine (IV) was converted into the tertiary base (VI) upon methylation with formaldehyde and formic acid; the same 1,3-dimethyl-3-β-dimethylaminoethyl-5-methoxyindolin-2-one (dehydroeserometolmethine) (VI) was obtained upon treating the sodium derivative of hydroxyindole (I) with chloroethyldimethylamine. After hydrolysis of the ester, rearrangement of compound (VI) by hydrobromic acid to 1,3-dimethyl-3-β-dimethylaminoethyl-5-hydroxyindolin-2-one (dehydroeserolinmethine)(VIII) took place, the sodium phenolate of which, with dimethylcarbamic acid chloroanhydride, gave the dimethylurethane of 1,3-dimethyl-3-β-dimethylaminoethyl-5-hydroxyindolin-2-one (X). Synthesis of 1,3-dimethyl-3-γ-dimethylaminopropyl-5-hydroxyindolin-2-one dimethylurethane (XI) was carried out in similar fashion, whereupon the nitrile (III) was obtained by condensation of hydroxyindole (I) with acrylonitrile in the presence of catalytic amounts of trimethylbenzylammonia ("triton B") base.

A study of the myotic effect of eserine analogs described in the present work as carried out on rabbits gave the following threshold concentration values for the substance in question*: hydrochloride (X) – 1: 5000; iodomethylate (X) – 1: 5000; hydrochloride (XI) – 1: 500.

EXPERIMENTAL

1) 1,3-Dimethyl-3-cyanomethyl-5-methoxyindolin-2-one (II). 15.8 g (2.92 gram atoms) of sodium in 500 ml of absolute alcohol was added over a period of 4 hours to a solution consisting of 45.0 g (1.00 mole) of 1,3-dimethyl-5-methoxyindolin-2-one in 200 ml of absolute alcohol and 50.0 g (2.81 moles) of chloroacetonitrile [2] stirred at 60°. After standing for 1 hour at the same temperature, the alcohol was distilled off in vacuo and the residue was dissolved, with shaking, in 120 ml of water and 200 ml of ether. The aqueous layer was extracted with ether, the ether solutions combined, dried with sodium sulfate and evaporated, and the residue was distilled. 50.3 g of viscous yellowish oil with b.p. 203-205° at 7 mm resulted. It was crystallized by grinding with a small amount of ether and then recrystallized from the same solvent. The yield of 1,3-dimethyl-3-cyanomethyl-5-methoxyindolin-2-one was 44.1 g (81%), m.p. 74.5-75.0°.

3.110 mg substance: 7.760 mg CO_2; 1.635 mg H_2O. 3.770 mg substance: 0.422 ml N_2 (24°, 735 mm).
Found %: C 68.04; H 5.90; N 12.44. $C_{13}H_{14}O_2N_2$. Calculated %: C 67.80; H 6.13; N 12.17.

2) 1,3-Dimethyl-3-β-aminoethyl-5-methoxyindolin-2-one (IV). 20.0 g of 1,3-dimethyl-3-cyanomethyl-5-methoxyindolin-2-one, a solution of saturated ammonia in 70 ml of absolute methanol at 0° and 2 g of a skeletal nickel catalyst were placed in a rocking autoclave of 200 ml capacity. The autoclave was filled with hydrogen to 120 atmospheres and was heated with shaking for 4 hours at 105-110°. After cooling, the solution was separated from catalyst by filtration, evaporated, and the residue distilled. 17.8 g (88%) of 1,3-dimethyl-3-β-aminoethyl-5-methoxyindolin-2-one resulted, b.p. 201-203° and 9 mm (compare [3]).

3.315 mg substance: 8.100 mg CO_2; 2.195 mg H_2O. 4.675 mg substance: 0.500 ml N_2 (25°, 734 mm).
Found %: C 66.63; H 7.41; N 11.83. $C_{13}H_{18}O_2N_2$. Calculated %: C 66.67; H 7.45; N 11.96.

Picrate was obtained from alcoholic solution and recrystallized from alcohol – yellow crystals with m.p. 161-162° (compare [3]).

Hydrogen iodide salt was obtained from an alcoholic solution of the base with hydrogen iodide and precipitation with ether. After recrystallizing from alcohol, it was found to be in the form of colorless crystals with m.p. 189-190°.

3.070 mg substance: 4.845 mg CO_2; 1.440 mg H_2O. 4.725 mg substance: 0.343 ml N_2 (20°, 725 mm).
Found %: C 43.04; H 5.25; N 8.07. $C_{13}H_{19}O_2N_2I$. Calculated %: C 43.09; H 5.29; N 7.73.

3) 1,3-Dimethyl-3-β-dimethylaminoethyl-5-methoxyindolin-2-one (dehydroesermetolmethine (VI).

A. From 1,3-Dimethyl-3-β-aminoethyl-5-methoxyindolin-2-one. 17.0 g of 1,3-dimethyl-3-β-aminoethyl-5-methoxyindolin-2-one was dissolved in 18 ml of 90% formic acid, 16 ml of 40% aqueous formaldehyde solution added, and the reaction mixture heated on a metal bath at 110-115° for 6 hours. The solution formed was evaporated in vacuo on a water bath, the residue made alkaline with 20% potassium hydroxide solution to phenolphthalein alkaline color, and the oil which separated was extracted with ether. The extract was washed with water, dried with sodium sulfate, the ether distilled off, and the residue distilled in vacuo. 13.4 g (70%) of 1,3-dimethyl-3-β-dimethylaminoethyl-5-methoxyindolin-2-one resulted with b.p. 210-215° at 20 mm.

B. From 1,3-Dimethyl-5-methoxyindolin-2-one. 20.0 g (1.00 mole) of 1,3-dimethyl-5-methoxyindolin-2-one and 1 ml of absolute alcohol were added to a suspension of 2.5 g (1.04 gram atoms) of pulverized sodium in 150 ml of absolute toluene and the mixture heated, with stirring, to boiling. After holding for 1 hour, 17.0 g (1.51 moles) of freshly-distilled chloroethyldimethylamine (b.p. 108-109°) was added over a period of 10 minutes, and stirring was continued at the same temperature for another hour. After cooling, the base was extracted with 10% hydrochloric acid (3 times with 30 ml portions), the toluene solution washed with a small volume of water, and the combined acid extract made alkaline with a 40% solution of sodium hydroxide. The oil which separated was extracted with ether, the extract dried with sodium sulfate, the ether distilled off, and the residue distilled.

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* Investigation of the compounds synthesized in the present work with respect to their physiological activity was carried out in the S. Ordzhonikidze All-Union Chemico-Pharmaceutical Research Institute by a senior scientific co-worker, I. M. Sharapov, directed by Prof. M. D. Mashkovsky, to whom the authors wish to express sincere appreciation.

22.8 g (83%) of 1,3-dimethyl-3-β-dimethylaminoethyl-5-methoxyindolin-2-one, with b.p. 140-143° at 2 mm was obtained.

Hydrochloride was obtained by saturation with dry hydrogen chloride of the base dissolved in an equal volume of alcohol. After recrystallization from ethanol, it was in the form of colorless crystals with m.p. 199.0-199.5°.

4.130 mg substance: 0.334 ml N_2 (17°, 750 mm). 3.885 mg substance: 0.314 ml N_2 (23°, 740 mm). Found %: N 9.40, 9.08. $C_{15}H_{23}O_2N_2Cl$. Calculated %: N 9.37.

Methyl iodide salt resulted from the addition of methyl iodide in excess to a solution of the base in dry acetone. After 10-15 minutes, dry ether was added to the point of light turbidity; on standing, colorless crystals precipitated. After recrystallization from absolute alcohol, the methyl iodide addition product had an m.p. of 156.0-156.5° (compare [4]).

Picrate was obtained from alcoholic solution and recrystallized from alcohol. It was in the form of bright-yellow crystals with m.p. 171.0-171.5°.

Methylpicrate was formed by heating an alcoholic solution of methyl iodide with picric acid excess. After recrystallization from a large volume of alcohol, it was in the form of lustrous yellow crystals with m.p. 194-195° (compare [4]).

4) 1,3-Dimethyl-3-β-dimethylaminoethyl-5-hydroxyindolin-2-one (dehydroeserolinmethine) (VIII). 5.0 g of 1,3-dimethyl-3-β-dimethylaminoethyl-5-methoxyindolin-2-one hydrochloride was heated with 25 ml of 50% hydrobromic acid on a metal bath at 135-140° for 2 hours. The hydrobromic acid was then distilled in vacuo on a water bath, the residue dissolved in methanol, and precipitated with ether. The mother liquors were evaporated and treated in a similar manner. After recrystallization from absolute alcohol, there resulted 5.16 g (94%) of 1,3-dimethyl-3-β-dimethylaminoethyl-5- hydroxyindolin-2-one hydrobromide, colorless crystals with m.p. 186.0-186.5°.

2.034 mg substance: 0.294 ml N_2 (21°, 748 mm). 3.820 mg substance: 0.274 ml N_2 (21°, 748 mm). Found %: N 8.33, 8.20. $C_{14}H_{21}O_2N_2Br$. Calculated %: N 8.51.

To separate the base, an alcoholic solution of the hydrobromide was mixed with an alcoholic solution of the calculated amount of potassium hydroxide, and then with a 10-fold volume of dry ether. The resulting crystals were filtered off. The filtrate was evaporated and the residue recrystallized from alcohol. 1,3-Dimethyl-3-β-dimethylaminoethyl-5-hydroxyindolin-2-one was in the form of colorless crystals with m.p. 170.0-170.5°; readily soluble in aqueous solutions of acids and alkalies, as well as in alcohol and chloroform, and poorly soluble in water and ether. The substance was best extracted from aqueous solutions with butyl alcohol.

4.765 mg substance: 0.461 ml N_2 (21°, 751 mm). 4.440 mg substance: 0.441 ml N_2 (21°, 751 mm). Found %: N 11.07, 11.36. $C_{14}H_{20}O_2N_2$. Calculated %: N 11.28.

Picrate was obtained from alcoholic solution. It crystallized from alcohol in the form of yellow needles with m.p. 177-178°.

The hydrochloride was obtained by the addition of an alcoholic solution of hydrogen chloride to an alcoholic solution of the base, and precipitated by ether. After recrystallization from alcohol, it was in the form of colorless crystals with m.p. 240.0-240.5°.

3.745 mg substance: 0.314 ml N_2 (21°, 751 mm). 3.008 mg substance: 0.255 ml N_2 (22°, 747 mm). Found %: N 9.59, 9.64. $C_{14}H_{21}O_2N_2Cl$. Calculated %: N 9.84.

5) Dimethylcarbamic Ester of 1,3-Dimethyl-3-β-dimethylaminoethyl-5-hydroxyindolin-2-one (dimethylurethane of dehydroeserolinmethine) (X). 3.00 g (1.00 mole) of 1,3-dimethyl-3-β-dimethylaminoethyl-5-hydroxyindolin-2-one was dissolved, with heat, in 10 ml of absolute methyl alcohol, and was mixed with a solution of 1.00 g (2.03 moles) of sodium methylate in 10 ml of methanol. The mixture was evaporated to dryness in vacuo, with heat from a water bath. The solid residue was finely-ground and suspended in 25 ml of absolute benzene. 1.50 g (1.53 moles) of dimethylcarbamic acid chloroanhydride was added and the reaction mass left for 48 hours at room temperature, after which it was heated for 2 hours on a water bath to complete reaction. The hot solution was filtered off from the sodium chloride and bromide, the precipitate washed with absolute benzene, the filtrate evaporated in vacuo, and the residue after distilling off the benzene, was shaken with 50 ml of absolute ether; thereupon white curds of precipitate (0.7 g) separated, which darkened and melted in the air. After the addition of an alcoholic

solution of hydrogen chloride to the ether filtrate, there precipitated a viscous precipitate of urethane hydrochloride, which then gradually solidified. After several precipitations with ether from alcoholic solution, we obtained 2.65 g (82%) of the dimethylcarbamic ester of 1,3-dimethyl-3-β-dimethylaminoethyl-5-hydroxyindolin-2-one hydrochloride, colorless crystals resulted with m.p. 211-212°.

3.500 mg substance: 0.348 ml N_2 (19°, 753 mm). 3.895 mg substance: 0.402 ml N_2 (21°, 751 mm). Found %: N 11.52, 11.81. $C_{17}H_{26}O_3N_3Cl$. Calculated %: N 11.81.

Picrate resulted from alcoholic solutions of the hydrochloride and picric acid. It crystallized from alcohol in the form of yellow needles with m.p. 193.5-194.0°.

To obtain the methyl iodide of the urethane, the hydrochloride was treated with an alcoholic solution of sodium methylate, the reaction mass diluted with a 10-fold volume of absolute ether, and removed from the sodium chloride by filtration. The filtrate was evaporated, the technical base (m.p. 83-84°) dissolved in dry ether, to which had been added several drops of alcohol, and methyl iodide added. The resulting precipitate was filtered off with suction, precipitated several times with ether from alcohol, and recrystallized from absolute alcohol. 0.10 g of sodium methylate, 0.5 ml of CH_3I and 0.68 g of the hydrochloride yielded 0.72 g of the dimethylcarbamic ester methyl iodide of 1,3-dimethyl-3-β-dimethylaminoethyl-5-hydroxyindolin-2-one, with m.p. 201-202°.

4.650 mg substance: 0.360 ml N_2 (21°, 751 mm). 3.945 mg substance: 0.306 ml N_2 (21°, 751 mm). Found %: N 8.86, 8.87. $C_{18}H_{28}O_3N_3I$. Calculated %: N 9.11.

6) 1,3-Dimethyl-3-β-cyanoethyl-5-methoxyindolin-2-one (III). 20.4 g (1.02 moles) of acrylonitrile was added to 72.0 g (1.00 mole) of 1,3-dimethyl-5-methoxyindolin-2-one solution and 3.6 g of 40% aqueous trimethylbenzylammonia base solution in 215 ml of dry dioxane, stirred, cooled with ice, the addition rate being such that the temperature of the reaction mixture did not rise above 15°. Stirring was continued for another 4 hours at room temperature, after which the dioxane was distilled in vacuo and the residue purified by crystallization from a mixture of ether and methyl alcohol. There resulted 81 g (88%) of 1,3-dimethyl-3-cyanoethyl-5-methoxyindolin-2-one with m.p. 89-90° and a b.p. of 178-180° at 1 mm; in mixture with 1,3-dimethyl-5-methoxyindolin-2-one, it gave an m.p. of 61-63°.

3.155 mg substance: 7.980 mg CO_2; 1.815 mg H_2O. 2.975 mg substance: 7.550 mg CO_2; 1.675 mg H_2O. 3.140 mg substance: 0.328 ml N_2 (21°, 725 mm). 3.090 mg substance: 0.329 ml N_2 (21°, 725 mm). Found %: C 68.97, 69.10; H 6.43, 6.30; N 11.56, 11.51. $C_{14}H_{16}O_2N_2$. Calculated %: C 68.82; H 6.60; N 11.47.

7) 1,3-Dimethyl-3-γ-aminopropyl-5-methoxyindolin-2-one (V). 20.0 g of 1,3-dimethyl-3-β-cyanoethyl-5-methoxyindolin-2-one was hydrogenated in the presence of 2 g of skeletal nickel catalyst under the conditions described for synthesis of 1,3-dimethyl-3-β-aminoethyl-5-methoxyindolin-2-one. 19.5 g (96 %) of 1,3-dimethyl-3-γ-aminopropyl-5-methoxyindolin-2-one, with b.p. 167-170° at 1 mm was obtained. For analysis, the material with b.p. 168° at 1 mm was taken.

3.070 mg substance: 7.650 mg CO_2; 2.180 mg H_2O. 3.095 mg substance: 7.690 mg CO_2; 2.220 mg H_2O. 2.175 mg substance: 0.221 ml N_2 (23°, 726 mm). 2.790 mg substance: 0.279 ml N_2 (22°, 727 mm). Found %: C 67.95, 67.75; H 7.94, 8.00; N 11.19, 11.07. $C_{14}H_{20}O_2N_2$. Calculated %: C 67.70; H 8.12; N 11.28.

Picrate formed by combining alcoholic solutions of the base and picric acid crystallized from aqueous methanol in the form of yellow needles with m.p. 162-163°.

2.405 mg substance: 0.372 ml N_2 (25°, 730 mm). 3.185 mg substance: 0.490 ml N_2 (25°, 730 mm). Found %: N 17.10, 16.92. $C_{20}H_{23}O_9N_5$. Calculated %: N 17.11

Hydrogen iodide salt was obtained by addition of an alcoholic solution of hydrogen iodide to an alcohol-ether solution of the base. After crystallization from absolute alcohol, it was in the form of colorless crystals with m.p. 185.5-186.0°.

2.895 mg substance: 4.770 mg CO_2; 1.470 mg H_2O. 3.025 mg substance: 4.930 mg CO_2; 1.600 mg H_2O. 3.675 mg substance: 0.245 ml N_2 (23°, 747 mm). 3.715 mg substance: 0.245 ml N_2 (23°, 748 mm). Found %: C 44.93, 44.44; H 5.68, 5.92; N 7.56, 7.48. $C_{14}H_{21}O_2N_2I$. Calculated %: C 44.68; H 5.63; N 7.44.

8) 1,3-Dimethyl-3-γ-dimethylaminopropyl-5-methoxyindolin-2-one (dehydrohomoeserometolmethine) (VII). A solution of 19.5 g of 1,3-dimethyl-3-γ-aminopropyl-5-methoxyindolin-2-one in 18 ml of 40% aqueous formaldehyde solution with 20 ml of 90% formic acid was heated for 6 hours on a metal bath at 115-120°. Upon further treatment, as described in Procedure A for the synthesis of 1,3-dimethyl-3-β-dimethylaminoethyl-5-methoxyindolin-2-one, there resulted 17.7 g (82 %) of 1,3-dimethyl-3-γ-dimethylaminopropyl-5-methoxyindolin-2-one, with b.p. 162-164° at 2 mm.

3.045 mg substance: 7.815 mg CO_2; 2.395 mg H_2O. 3.035 mg substance: 7.710 mg CO_2; 2.390 mg H_2O. 2.820 mg substance: 0.255 ml N_2 (25°, 754 mm). 2.805 mg substance: 0.255 ml N_2 (24°, 741 mm). Found %: C 69.99, 69.27; H 8.80, 8.82; N 10.28, 10.19. $C_{16}H_{24}O_2N_2$. Calculated %: C 69.52; H 8.76; N 10.14.

Picrate, obtained in the usual manner, was obtained as yellow crystals, m.p. 139-140° after recrystallization from alcohol.

The hydrogen iodide derivative from alcoholic solutions of the base and hydrogen iodide. It crystallized from absolute alcohol in the form of colorless crystals with m.p. 181.0-181.5°; a mixture with hydrogen iodide salt of 1,3-dimethyl-3-γ-aminopropyl-5-methoxyindolin-2-one melted at 153-156°.

3.640 mg substance: 0.216 ml N_2 (21°, 747 mm). 3.500 mg substance: 0.225 ml N_2 (22°, 733 mm). Found %: N 6.74, 7.17. $C_{16}H_{25}O_2N_2I$. Calculated %: N 6.94.

9) 1,3-Dimethyl-3-γ-dimethylaminopropyl-5-hydroxyindolin-2-one (dehydrohomoeserolinmethine) (IX). A solution of 15.0 g of 1,3-dimethyl-3-γ-dimethylaminopropyl-5-methoxyindolin-2-one in 75 ml of 50 % hydrobromic acid was heated for 2 hours on a metal bath at 140-145°, the reaction mixture then evaporated on a water bath, and the residue dissolved in a small volume of 20% potassium hydroxide solution. The solution was clarified by addition of 40% sodium bisulfite solution, and then made weakly alkaline to litmus paper. The base was extracted with butyl alcohol, the extract washed with water, and the butanol distilled off completely in vacuo. The residue upon grinding with ether crystallized. It was filtered by suction, washed with methanol and ether mixture, and recrystallized from methyl alcohol. 7.4 g (52%) of 1,3-dimethyl-3-γ-dimethylaminopropyl-5-hydroxyindolin-2-one resulted – colorless crystals with m.p. 145-147°. After a second recrystallization, the substance had an m.p. of 147-148°.

2.980 mg substance: 7.505 mg CO_2; 2.245 mg H_2O. 3.090 mg substance: 7.800 mg CO_2; 2.330 mg H_2O. 3.020 mg substance: 0.294 ml N_2 (23°, 720 mm). 2.885 mg substance: 0.274 ml N_2 (25°, 730 mm). Found %: C 68.68, 68.83; H 8.43, 8.44; N 10.63, 10.45. $C_{15}H_{22}O_2N_2$. Calculated %: C 68.66; H 8.46; N 10.68.

Picrate was obtained by means of alcoholic picric acid, and recrystallized from alcohol – yellow needles with m.p. 184.5-185.0°.

The hydrogen iodide salt was obtained by mixing alcoholic solutions of the base and of hydrogen iodide, followed by precipitation with ether. After recrystallization from absolute alcohol, it represented colorless crystals with m.p. 192-193°; its mixture with the hydrogen iodide salt of 1,3-dimethyl-3-γ-dimethylaminopropyl-5-methoxy indolin-2-one had an m.p. of 160-162°.

3.050 mg substance: 5.130 mg CO_2; 1.585 mg H_2O. 3.005 mg substance: 5.090 mg CO_2; 1.630 mg H_2O. 3.370 mg substance: 0.215 ml N_2 (25°, 745 mm). 3.635 mg substance: 0.235 ml N_2 (25°, 745 mm). Found %: C 45.90, 46.19; H 5.81, 6.06; N 7.16, 7.26. $C_{15}H_{23}O_2N_2I$. Calculated %: C 46.16; H 5.94; N 7.17.

10) Dimethylcarbamic ester of 1,3-dimethyl-3-γ-dimethylaminopropyl-5-hydroxyindolin-2-one (dimethylurethane of dehydrohomoeserolinmethine) (XI). The phenolate was prepared from 3.27 g (1.00 mole) of 1,3-dimethyl-3-γ-dimethylaminopropyl-5-hydroxyindolin-2-one and 0.667 g (0.99 mole) of CH_3ONa in 15 ml of absolute methyl alcohol, which was then suspended in 35 ml of absolute benzene and treated with 2.00 g (1.49 moles) of dimethylcarbamic acid chloroanhydride. Reaction and isolation of the compound was carried out by a method described for synthesis of the dimethylurethane of dehydroeserolinmethine. There resulted 0.6 g of a darkening substance which melted in the air, and which was not investigated further, plus 3.60 g of 5-hydroxyindolin-2-one, with m.p. 103-105°.

3.045 mg substance: 0.314 ml N_2 (25°, 736 mm). 3.345 mg substance: 0.353 ml N_2 (23°, 735 mm). Found %: N 11.43, 11.78. $C_{18}H_{28}O_3N_3Cl$. Calculated %: N 11.35.

The picrate was obtained from an alcoholic solution of the hydrochloride and picric acid; it crystallized from alcohol in the form of yellow crystals with m.p. 134-135°.

SUMMARY

Synthesis of hydroxyindolic analogs of the alkaloid eserine, has been achieved — dimethylcarbamic esters of 1,3-dimethyl-3-β-dimethylaminoethyl-5-hydroxyindolin-2-one and of 1,3-dimethyl-3-γ-dimethylaminopropyl-5-hydroxyindolin-2-one.

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A CATALYTIC METHOD FOR SYNTHESIS OF α-METHYLNAPHTHALENE FROM α-CHLOROMETHYLNAPHTHALENE

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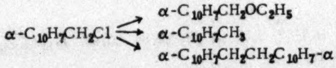
The isolation of α-methylnaphthalene from hard coal tar without impurities, offers great difficulties [1], and so, in those cases where pure α-methylnaphthalene is required, organic synthetic methods are used. The simplest of methods for α-methylnaphthalene can be considered to be the reduction of α-chloromethylnaphthalene, which can be carried out both catalytically and non-catalytically.

Of the non-catalytic methods to be found in the literature, reduction by means of zinc and hydrochloric acid is to be recommended [2], the yield of α-methylnaphthalene reaching 68%, but this method is applicable only for work with small quantities [3]. The literature contains only brief directions for catalytic procedures for reducing α-chloromethylnaphthalene. Vavon [4], in studying the synthesis of aromatic chloromethylated compounds, among them α-chloromethylnaphthalene, indicated the possibility of reducing them to the corresponding hydrocarbon by the use of hydrogen in the presence of platinum black. The yield of hydrocarbons reached 90-95%. Other investigators have described [5] the catalytic reduction of α-chloromethylnaphthalene in the presence of palladium on strontium carbonate. To tie up the hydrogen chloride evolving during reaction, sodium alcoholate was added. As a result, impure α-methylnaphthalene was obtained; the authors assume that it also contained α-naphthylcarbinol.

In the present work on hydrogenation of α-chloromethylnaphthalene, Raney nickel catalyst or palladium black was used; the reaction was studied in greater detail with nickel catalyst, and in this case hydrogenation was carried out under a variety of conditions. Hydrogenation experiments carried out without addition of a substance to neutralize the hydrogen chloride did not produce positive results, because absorption of hydrogen rapidly ceased due to poisoning of the catalyst. Upon carrying out the reaction in presence of alkali in alcholic solution, regardless of whether pressure was used or not, there was also formed in addition to α-methylnaphthalene, the ethyl ester of α-naphthylcarbinol of di(α-naphthyl)-ethane.



$$\alpha\text{-}C_{10}H_7CH_2Cl \rightarrow \begin{cases} \alpha\text{-}C_{10}H_7CH_2OC_2H_5 \\ \alpha\text{-}C_{10}H_7CH_3 \\ \alpha\text{-}C_{10}H_7CH_2CH_2C_{10}H_7\text{-}\alpha \end{cases}$$

Inasmuch as formation of the ethyl ester of α-naphthylcarbinol might be explained as due to the effect of alcoholic alkali, in place of alkali, anhydrous sodium acetate in alcoholic solution was used. As the result, under these conditions formation of the ethyl ester of α-naphthyl carbinol was either not observed at all, or it proceeded to a very minor degree. The yield of α-methylnaphthalene amounted to 85% of theory. Di-(α-naphthyl)-ethane was found to be a constant companion in the reaction, but its amount was small. The hydrogenation reaction was more convenient to carry out under elevated pressure. The inconvenience of the method was the low solubility of anhydrous sodium acetate in 96% ethyl alcohol, because of which the authors set up experiments on hydrogenation of α-chloromethylnaphthalene in the presence of alcoholic alkali and ethyl acetate. Thus, homogeneity of the medium was attained, and excess alkalinity removed rapidly by progressive hydrolysis of the ethyl acetate to form sodium acetate. Under these conditions, the yield of α-methylnaphthalene amounts to 85-87% of theory. In none of these cases was formation of the ethyl ester of α-naphthylcarbinol observed. The only by-product of the reaction was found to be the di-(α-naphthyl)-ethane. The same results were obtained by hydrogenation of α-chloromethylnaphthalene in the presence of palladium black, alcoholic alkali and ethyl acetate under atmospheric pressure. By hydrogenating α-chloromethylnaphthalene in the presence of sodium acetate or in a medium of ethyl acetate in alcoholic alkali, it was possible to obtain in the laboratory α-methylnaphthalene in any desired amount. The same method is adaptable to larger scale production. However, the question of the reaction course in the presence of alkali in a solution which consists of ethyl alcohol and ethyl acetate mixed, and the role of ethyl acetate requires a more extensive and thorough study.

EXPERIMENTAL

1. Hydrogenation of α-Chloromethylnaphthalene in the Presence of Nickel Catalyst and in Alcoholic Alkali

a) At atmospheric pressure. 17.3 g of α-chloromethylnaphthalene in 200 ml of alcoholic alkali and 10 g of catalyst in 20 ml of 96 % ethyl alcohol, were shaken in a hydrogen medium. After completion of absorption of the theoretical amount of hydrogen, the solution was filtered and the alcohol distilled off. The substance remaining was dissolved in ether, the ether solution washed with water, and dried with sodium sulfate. After distilling off the ether, the substance was distilled in vacuo.

α-Methylnaphthalene with b.p. 110-113° at 9 mm, resulted in the amount of 8.3 g (59 %), (picrate m. p. 141-141.5°); 9.5 g (34 %) of a higher boiling fraction, and an oily residue which crystallized upon standing, also were obtained.

b) Under elevated pressure. A solution of 50 g of α-chloromethylnaphthalene in alcoholic alkali (14.5 g of NaOH in 350 ml of ethyl alcohol) and 10 g of catalyst in 50 ml of alcohol were placed in an autoclave. The autoclave was filled with hydrogen to a pressure of 27.5 atm. Hydrogenation proceeded at room temperature with the autoclave rotating.

After completion of the reaction, and standard treatment, a substance was obtained which did not contain halogen (Beilstein test); it was distilled: 1st fraction, 98-110° at 6 mm – 26.9 g (67 %); 2nd fraction, b.p. 110-138° at 6 mm – 7.1 g. The residue in the flask, amounting to 2.3 g, crystallized. Upon repetition of the distillation, the following fractions were isolated:

1st: a substance with b.p. 96-103° at 5 mm, representing α-methylnaphthalene; picrate m.p. 142°. To determine the molecular refraction of α-methylnaphthalene, the substance which boiled at 96-103° at 5 mm was distilled over sodium; b.p. 97-98° at 5.5 mm; d_4^{20} 1.0187; n_D^{20} 1.6170; MR_D 48.83; calculated 49.07.*

2nd: a substance with b.p. 130-135° at 5.5 mm, representing the ethyl ester of α-naphthyl carbinol.

Di-(α-naphthyl)-ethane. There resulted from the residue which remained in the flask after the first distillation of substance (2.3 g) and washing with benzene, a white crystalline substance, which was soluble in benzene on heating, insoluble in alcohol, m.p. 155-158°; after two recrystallizations from benzene, the substance melted at 164°. Melting point, solubility and analytical data indicated that this substance was di-(α-naphthyl)-ethane.

Found %: C 93.40, 93.67; H 6.46, 6.39. $C_{22}H_{18}$. Calculated %: C 93.56; H 6.44.

Ethyl Ester of α-Naphthyl-carbinol. The higher fraction with b.p. 100-140° at 6-7 mm was distilled in vacuo, and the substance with b.p. 133-136° at 6.7 mm was taken, which was again distilled in vacuo; b.p. was 134-136° at 6 mm.**

Found %: C 83.52, 83.89; H 7.67, 7.57; OC_2H_5 23.84, 23.92. $C_{10}H_7CH_2OC_2H_5$. Calculated %: C 83.83; H 7.57; OC_2H_5 24.19.

2. Hydrogenation of α-Chloromethylnaphthalene in the presence of Nickel catalyst and of anhydrous sodium acetate.***

a) At atmospheric pressure. 10 g of α-chloromethylnaphthalene, an alcoholic solution of anhydrous**** sodium acetate (7.3 g CH_3COONa in 100 ml of 96 % alcohol) containing some undissolved sodium acetate, and 10 g of nickel catalyst, were hydrogenated by standard procedure.

After completion of hydrogen absorption and separation of the catalyst, the solution showed a weakly-alkaline reaction to litmus paper. After the usual treatment, 6.3 g (78.7 %) of α-methylnaphthalene with b.p. 128° at 28 mm, and 0.9 g of di-(α-naphthyl)-ethane residue which crystallized in the distilling flask, were obtained.

b) With elevated pressure. A solution of 50 g of α-chloromethylnaphthalene and 25 g of anhydrous sodium acetate in 500 ml of ethyl alcohol were placed in the autoclave and 10 g of nickel catalyst in 20 ml of alcohol added. The autoclave was filled with hydrogen to 28 atmospheres. Hydrogenation was continued for about one hour. After the usual treatment, a substance was obtained in the form of an oil, which did not contain halogen. The substance was distilled in vacuo. α-Methylnaphthalene distilled at 104° at 10 mm, 34.1 g (85%) resulting; 5.2 g of a higher-boiling residue was left behind in the flask, upon distillation of which 3.25 g of substance with b.p. 180-185° at 28 mm, or 134-135° at 6 mm (the ethyl ester of α-naphthylcarbinol) resulted, along with 0.97 g of a rapidly crystallizing residue, m.p. 162° (from benzene) [di-(α-naphthyl)-ethane].

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* The refraction was calculated, taking into account exaltation = 2.8.

** According to the literature data [6], b.p. is 144.5° at 11 mm.

*** Investigation by T. S. Safonova.

**** It was determined by the authors that use of ordinary sodium acetate complicated processing of the reaction product, as a result of which, the yield of α-methylnaphthalene was decreased.

3. Hydrogenation of α-Chloromethylnaphthalene in the Presence of Nickel Catalyst, Alcoholic Alkali and Ethyl Acetate.

a) At atmospheric pressure. 10 g of α-chloromethylnaphthalene, 15 ml of ethyl acetate, 100 ml of alcoholic alkali (3.7 g of sodium hydroxide in 100 ml of 96% alcohol), and 10 g of nickel catalyst were taken for reaction. Hydrogenation was carried out as usual. After completion of reaction, the solution showed a weakly alkaline reaction to litmus. 6.9 g of α-methylnaphthalene (86.2% of theory), b.p. 126-128° at 28 mm and 1 g of di-(α-naphthyl)-ethane, m.p. 162° (from benzene) resulted.

b) At elevated pressure. A solution of 50 g α-chloromethylnaphthalene in alcoholic alkali (18.5 g of NaOH in 450 ml of 96% ethyl alcohol) and 75 ml of ethyl acetate were placed in an autoclave, whereupon 10 g of catalyst in 20 ml of alcohol was introduced. Hydrogenation was carried out as usual at 28 atm. pressure. After completion of the reaction, the filtrate showed an acid reaction to litmus, neutral to Congo red.

33.9 g of α-methylnaphthalene with b.p. 96° at 5 mm (85%) resulted, and a crystalline substance with m.p. 156-158°. After crystallization from benzene, m.p. was 164°.

4. Hydrogenation of α-Chloromethylnaphthalene in the Presence of Palladium Black, Alcoholic Alkali and Ethyl Acetate.

2 g of palladium chloride was dissolved in a small amount of water, 10-15 ml of alcohol added, and the palladium chloride reduced by hydrogen to form palladium black. The liquid was poured off from the resulting palladium black into a beaker containing 20 g of α-chloromethylnaphthalene dissolved in a mixture of 30 ml ethyl acetate and 200 ml alcoholic alkali (7.2 g of NaOH and 200 ml of 80% ethyl alcohol).

13.5 g of α-methylnaphthalene (84.4 %) was obtained. B.p. 95-97° at 5 mm.

SUMMARY

1. By hydrogenation of α-chloromethylnaphthalene in the presence of Raney nickel and alcoholic alkali, the following are formed: α-methylnaphthalene (60-70%), the ethyl ester of α-naphthylcarbinol and di(α-naphthyl)-ethane.

2. By hydrogenation of α-chloromethylnaphthalene in alcoholic medium in the presence of Raney nickel and anhydrous sodium acetate, α-methylnaphthalene results in about 85% yield.

3. α-Methylnaphthalene results in 85-87% yield by hydrogenation of α-chloro-methylnaphthalene in the presence of catalyst (Raney nickel or palladium black), alcoholic alkali and ethyl acetate.

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INTERACTION OF ANABASINE WITH ORGANIC ACIDS

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In the preceding work [1], the authors examined interaction of anabasine with mineral acids, and it was demonstrated that isolation of the salts in a crystalline form occurs only in organic solvents, the best of which was found to be acetone. Having taken on the problem of examining interaction of anabasine with acids of various types and concentrations, the authors in the present article give results for interaction of anabasine with organic acids.

EXPERIMENTAL

Anabasine obtained from technical anabasine sulfate had n_D^{20} 1.5440 b.p. 106-110° at 4 mm.

All salts were analyzed for their acids content, which, for a majority of cases, was determined by conductometric titration with alkali hydroxide by the visual apparatus of A. P. Toropov [2]. Nitrogen was determined in stable, non-hygroscopic salts according to Dumas.

Synthesis and analysis of hygroscopic salts was carried out in a special apparatus in which the compound was completely isolated from the surrounding atmosphere [3].

The acid used for the work was purified and dehydrated beforehand.

Synthesis of Anabasine Formate. The compound resulted from direct mixing of anabasine and the acid in equimolecular quantities. Reaction proceeded with evolution of heat, and led to the formation of a thick, viscous mass, from which it was difficult to induce crystallization of the compound. The mass which crystallized was washed with gasoline or benzene, as the result of which it again converted to a thick mass, which again crystallized upon standing over calcium chloride in a desiccator. The crystals which formed melted in air, but again separated over calcium chloride. The resulting compound was very hygroscopic, darkening in air, a white crystalline compound, readily soluble in water, alcohol, ether and acetone. It was not possible to recrystallize it from these solvents because of its high solubility.

0.0356 g sub.: 2.3 ml 0.07548 N $Ba(OH)_2$. 0.0265 g sub.: 1.7 ml 0.07548 N $Ba(OH)_2$. Found %: HCOOH 22.45, 22.29. $C_{10}H_{14}N_2 \cdot HCOOH$. Calculated %: HCOOH 22.37.

Synthesis of Anabasine Acetate. As in the preceding case, upon mixing equimolecular quantities of anabasine and acetic acid, strong heat evolution resulted, and a thick, viscous mass formed, which after standing 24 hours, crystallized. The white crystals, washed with acetone, were dried in a vacuum desiccator, after which they possessed an m.p. of 88°. The resulting salt was hygroscopic.

0.0362 g sub.: 2.15 ml 0.07548 N $Ba(OH)_2$. 0.0310 g sub.: 1.85 ml 0.07548 N Ba(OH)2. Found %: CH_3COOH 26.92, 27.11. $C_{10}H_{14}N_2 \cdot CH_3COOH$. Calculated %: CH_3COOH 27.00.

Synthesis of Anabasine Butyrate. Anabasine butyrate also resulted with considerable heat evolution on interaction of equimolecular quantities of acid and anabasine. The resulting light-brown viscous mass crystallized after 24 hours. Upon washing the resulting crystals with gasoline or benzene, they converted into an oily liquid, yellow in color, which, upon standing over calcium chloride, again solidified in the form of white crystals. The resulting salt was very hygroscopic and difficult to wash free of impurities. It failed to crystallize out from available solvents.

0.0522 g sub.: 2.8 ml 0.07548 N $Ba(OH)_2$. 0.0444 g sub.: 2.3 ml 0.07548 N $Ba(OH)_2$. Found %: C_3H_7COOH 34.48, 35.67. $C_{10}H_{14}N_2 \cdot C_3H_7COOH$. Calculated %: C_3H_7COOH 35.19.

Synthesis of Anabasine Isovalerate. The compound resulted by direct interaction of equimolecular quantities of anabasine and acid. After 24 hours a solid compound was isolated from the solidified mass, which failed to recrystallize. After washing out the impurities with benzene, the crystals converted to a yellowish oily liquid from which, after standing in a desiccator over calcium chloride, it separated as white hygroscopic crystals.

0.0496 g sub.: 1.8 ml 0.1026 N KOH. 0.0722 g sub.: 2.7 ml 0.1026 N KOH. Found %: iso-C_4H_9COOH 38.01, 39.17. $C_{10}H_{14}N_2 \cdot C_4H_9COOH$. Calculated %: C_4H_9COOH 38.63.

Synthesis of Anabasine Oxalate. The oxalate was obtained from an acetone solution of anabasine and the anhydrous acid. Upon mixing the acetone solution, depending upon the ratio of acid to anabasine, three different types of salts separated: $2C_{10}H_{14}N_2 \cdot H_2C_2O_4$ with b.p. 210°, $C_{10}H_{14}N_2 \cdot H_2C_2O_4$ with b.p. 199° and $C_{10}H_{14}N_2 \cdot 2H_2C_2O_4$ with b.p. 81°. All three compounds were white substances, stable in air, readily soluble in water and poorly soluble in organic solvents. Prior to analyses, the salts were filtered by suction on a filter, washed thoroughly with acetone, and then dried in the air. The oxalic acid content in the compound was determined by titration with permanganate solution.

0.1300 g sub.: 15.3 ml N_2 (15°, 732 mm). 0.2408 g sub.: 28.5 ml N_2 (15°, 732 mm). 0.190 g sub.: 1.5 ml 0.0611 N $KMnO_4$. 0.0037 g sub.: 0.3 ml 0.0588 N $KMnO_4$. Found %: N 13.2, 13.27; C_2O_4 21.22, 21.00. $2C_{10}H_{14}N_2 \cdot C_2H_2O_4$. Calculated %: N 13.52; C_2O_4 21.23.

0.0079 g sub.: 0.85 ml N_2 (29°, 723 mm). 0.0139 g sub.: 1.5 ml N_2 (28°, 723 mm). 0.0050 g sub.: 0.25 ml 0.1540 N $KMnO_4$. 0.0040 g sub.: 0.50 ml 0.0610 N $KMnO_4$. Found %: N 11.10, 11.19; C_2O_4 33.88, 33.61. $C_{10}H_{14}N_2 \cdot C_2H_2O_4$. Calculated %: N 11.11; C_2O_4 34.09.

0.3412 g sub.: 26.8 ml N_2 (21°, 728 mm). 0.3417 g sub.: 26.5 ml N_2 (22°, 727 mm). 0.0702 g sub.: 5.3 ml 0.1540 N $KMnO_4$. 0.0276 g sub.: 5.5 ml 0.0588 N $KMnO_4$. Found %: N 8.52, 8.35; C_2O_4 51.18, 51.58. $C_{10}H_{14}N_2 \cdot 2C_2H_2O_4$. Calculated %: N 8.19; C_2O_4 51.42.

Synthesis of Anabasine Malonate. Upon mixing solutions of anabasine and malonic acid, a white crystalline compound separated, readily soluble in water and acetone. The salt was washed with benzene and dried over calcium chloride in a desiccator. M.p. 66°.

0.0159 g sub.: 0.97 ml 0.07548 N $Ba(OH)_2$. 0.0118 g sub.: 0.73 ml 0.07548 N $Ba(OH)_2$. Found %: $C_3H_4O_4$ 23.95, 24.29. $2C_{10}H_{14}N_2 \cdot C_3H_4O_4$. Calculated %: $C_3H_4O_4$ 24.28.

Synthesis of Anabasine Succinate. Upon mixing acetone solutions of succinic acid and anabasine in the ratio 1:2, a white crystalline compound precipitated. It was hygroscopic and melted readily in the air; its synthesis, therefore, and its analysis, were carried out in a special apparatus.

0.0231 g sub.: 1.4 ml 0.07548 N $Ba(OH)_2$. 0.0576 g sub.: 3.4 ml 0.07548 N $Ba(OH)_2$. Found %: $C_4H_6O_4$ 27.01, 26.30. $2C_{10}H_{14}N_2 \cdot C_4H_6O_4$. Calculated %: $C_4H_6O_4$ 26.67.

Synthesis of Anabasine Tartrate. As the result of mixing equimolecular quantities of d-tartaric acid and anabasine, there resulted from the viscous mass produced, after 24 hours standing, a precipitate, stable in air, white and crystalline. It was washed with acetone and dried in air, whereupon the m.p. was 115°.

0.5488 g sub.: 42.7 ml N_2 (26°, 723 mm). 0.0756 g sub.: 6.7 ml N_2 (29°, 724 mm). 0.0626 g sub.: 0.90 ml 0.4420 N $Ba(OH)_2$. 0.0429 g sub.: 0.62 ml 0.4420 N $Ba(OH)_2$. Found %: N 8.16, 9.05; $C_4H_6O_6$ 47.66, 47.92. $C_{10}H_{14}N_2 \cdot C_4H_6O_6$. Calculated %: N 8.97; $C_4H_6O_6$ 48.03.

Upon interacting d-tartaric acid with anabasine in acetone solution, a white solid of the composition, $2C_{10}H_{14}N_2 \cdot H_2C_4H_4O_6$.

0.2869 g sub.: 15.7 ml 0.07548 N $Ba(OH)_2$. 0.0309 g sub.: 1.75 ml 0.07548 N $Ba(OH)_2$. Found %: $C_4H_6O_6$ 30.98, 32.07. $2C_{10}H_{14}N_2 \cdot C_4H_6O_6$. Calculated %: $C_4H_6O_6$ 31.61.

Synthesis of Anabasine Citrate. This salt was prepared by mixing acetone solutions of anabasine and citric acid in a 3:1 ratio. The white flaky compound which precipitated was hygroscopic, melting readily in air, and readily soluble in water; it was therefore, prepared in a special apparatus, washed with acetone and after drying in vacuo was analyzed.

0.0968 g sub.: 5.8 ml 0.07548 N $Ba(OH)_2$. 0.0387 g sub.: 2.3 ml 0.07548 N $Ba(OH)_2$. Found %: $C_6H_8O_7$ 28.96, 28.72. $3C_{10}H_{14}N_2 \cdot C_6H_8O_7$. Calculated %: $C_6H_8O_7$ 28.29.

Synthesis of Anabasine β-Naphthalenesulfonate. Upon mixing acetone solutions of the acid and anabasine, in a one-to-one ratio, two compounds were isolated, of the following composition: $C_{10}H_{14}N_2 \cdot C_{10}H_7SO_3H$ with b.p. 139° and $C_{10}H_{14}N_2 \cdot 2C_{10}H_7SO_3H$ with b.p. 121°. The first salt resulted from a slight excess of anabasine, and the second by small acid excess. Both salts turned out to be crystalline compounds, stable in air, readily soluble in water and in excess acid.

0.0475 g sub.: 3.6 ml N_2 (29°, 721 mm). 0.0500 g sub.: 3.8 ml N_2 (30°, 721 mm). 0.0570 g sub.: 0.35 ml 0.4420 N $Ba(OH)_2$. 0.0460 g sub.: 0.28 ml 0.4420 N $Ba(OH)_2$. Found %: N 7.80, 7.84; $C_{10}H_7SO_3H$ 56.50, 56.40. $C_{10}H_{14}N_2 \cdot C_{10}H_7SO_3H$. Calculated %: N 7.57; $C_{10}H_7SO_3H$ 56.87.

0.1365 g sub.: 6.2 ml N_2 (27°, 723 mm). 0.1379 g sub.: 6.4 ml N_2 (32°, 723 mm). 0.0384 g sub.: 0.236 ml 0.4420 N $Ba(OH)_2$. 0.0630 g sub.: 0.488 ml 0.4420 N $Ba(OH)_2$. Found %: N 4.74, 4.70; $C_{10}H_7SO_3H$ 71.20, 71.25. $C_{10}H_{14}N_2 \cdot 2C_{10}H_7SO_3H$. Calculated %: N 4.85; $C_{10}H_7SO_3H$ 71.96.

EVALUATION OF RESULTS

Anabasine salts with monobasic acids possess high hygroscopicity. It is apparently due to this fact that the anabasine compound with formic acid was not isolated in solid form when the anabasine-formic acid system was studied by methods of physico-chemical analysis [4].

Hygroscopicity of anabasine compounds with organic acids depends upon their composition and upon the nature of the acid. They all crystallize over $CaCl_2$ in a desiccator. The anabasine compound with sulfuric and phosphoric acids did not crystallize under the same conditions, a fact which should be attributed to hygroscopicity of the acids themselves.

Upon examining salts of the anabasine compound with organic acids, there can be observed a regular order in their melting points. If the melting points for anabasine salts of various types are compared with the same acid, then those salts with the highest melting points will be the ones in which anabasine plays a role of monoacidic base, for example, the salts of anabasine with oxalic and β-naphthalenesulfonic acid. When the anabasine acts as a diacidic base, salts of lower melting points are formed.

Salts of anabasine with acids were prepared in a majority of cases by the authors from acetone solutions, and with only a few acids, such as formic and acetic, were salts formed with anabasine by direct interaction. The capacity of acids to form salts with anabasine in acetone solution depends upon their strength [5]. A strong acid such as β-naphthalenesulfonic acid, or an acid of average strength —oxalic acid— in acetone solution with anabasine forms several stable compounds. Very weak acids —salicyclic and benzoic— do not form salts with anabasine in acetone solution.

SUMMARY

1. Equimolecular, hygroscopic compounds of anabasine with formic, acetic, butyric and isobutyric acids have been prepared.

2. Crystalline compounds of anabasine with oxalic acid, of the composition as follows: $2C_{10}H_{14}N_2 \cdot C_2H_2O_4$, $C_{10}H_{14}N_2 \cdot C_2H_2O_4$ and $C_{10}H_{14}N_2 \cdot 2C_2H_2O_4$, have been synthesized, with malonic acid $2C_{10}H_{14}N_2 \cdot C_3H_4O_4$ and with citric acid, of the composition $2C_{10}H_{14}N_2 \cdot C_4H_6O_4$.

3. An anabasine compound with tartaric acid of the composition $2C_{10}H_{14}N_2 \cdot C_4H_6O_6$ and $C_{10}H_{14}N_2 \cdot C_4H_6O_6$ has been obtained; and with citric acid, of the composition $3C_{10}H_{14}N_2 \cdot C_6H_8O_7$.

4. Crystalline compounds of anabasine with β-naphthalenesulfonic acid, of the composition $C_{10}H_{14}N_2 \cdot C_{10}H_7SO_3H$ and of the composition $C_{10}H_{14}N_2 \cdot 2C_{10}H_7SO_3H$ have been obtained.

5. It has been observed that compounds of anabasine with organic acids behave predominately as a monoacidic base.

6. It has been demonstrated that acetone is a better solvent for the synthesis of salts of anabasine with acids, and that the formation of crystalline compounds is in direct relation to the strengths of these acids in acetone.

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INTERACTION OF ANABASINE WITH INORGANIC ACIDS

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In an earlier published work [1] the authors demonstrated that the alkaloid, anabasine, can form salts with mineral acids, representing stable crystalline substances. Upon interacting anabasine with hydrogen chloride and nitric acid, equimolecular compounds were isolated in crystalline form, while anabasine has been found to be a diacidic base. In the present work, the authors have engaged the problem of clarifying the behavior of anabasine as a base when it reacts with inorganic acids of various strengths and types.

Anabasine used for the work was isolated from technical anabasine sulfate. The resulting anabasine boiled at 106-110° (4 mm), n_D^{20} 1.5440.

All stable salts were analyzed for nitrogen content and for acid content. Analysis for nitrogen was carried out according to Dumas. The quantity of acid in the salt was determined by conductometric titration with barium hydroxide by means of the visual apparatus of A. P. Toropov [2], or by potentiometric titration with silver nitrate. For hygroscopic salts which melted in the air, analysis was carried out in a special apparatus in which the substance was completely isolated from the surrounding medium [3].

EXPERIMENTAL

Synthesis of Anabasine Hydrobromide. The salt of anabasine and hydrogen bromide separated in the form of needle crystals upon mixing equimolecular acetone solutions of anabasine and hydrogen bromide, cooled in ice, and was purified by a procedure known in the literature [4]. The salt was stable in air, readily soluble in water and in excess hydrogen bromide. After thorough washing with acetone and drying, it had a m.p. of 181°. The salt could be recrystallized from acetone, which was difficult however, due to low solubility in this solvent.

Found %: N 11.40, 11.26; Br 32.26, 33.17. $C_{10}H_{14}N_2 \cdot HBr$. Calculated %: N 11.52; Br 32.86.

Synthesis of Anabasine Hydriodide. As in the preceding case, a compound of anabasine and hydriodic acid resulted upon mixing equimolecular quantities of anabasine and hydrogen iodide dissolved in acetone, cooled with ice. The hydrogen iodide was prepared and purified by a method known in the literature [4]. The anabasine hydriodide was in the form of a fine, white crystalline powder, stable in air and readily soluble in water and excess acid. Recrystallization of this salt from acetone was hindered because of its poor solubility. The salt thoroughly washed with acetone and dried in air had a m.p. of 253°.

Found %: N 9.23, 9.39; I 43.37, 43.44. $C_{10}H_{14}N_2 \cdot HI$. Calculated %: N 9.66; I 43.59.

It should be mentioned that the crystalline hydriodide, as well as the hydrobromide, separates only upon mixing cooled acetone solutions containing equimolecular quantities of anabasine and acid. At other ratios the crystalline compound failed to separate.

Synthesis of Anabasine Sulfate. If sulfuric acid is carefully added, with continuous stirring, to a solution of anabasine in acetone, then the anabasine sulfate separates in the form of white, crystalline flakes, dissolving in excess of acid. Upon filtering this salt in air, it becomes viscous because of hygroscopicity, and cannot be removed from the filter. However, upon isolating the substance from surrounding medium in a special apparatus, it was possible to isolate it and to analyze it. Anabasine sulfate resulted upon addition of sulfuric acid to an anabasine solution for the calculated ratio of 1:1. Upon interacting one acid molecule with two molecules of anabasine a yellow viscous mass separated. Because of its hygroscopicity, the anabasine sulfate was analyzed only for the acid content.

Found %: H_2SO_4 37.01, 36.93. $C_{10}H_{14}N_2 \cdot H_2SO_4$. Calculated %: H_2SO_4 37.68.

Synthesis of Anabasine Phosphate. Chemically-pure orthophosphoric acid was taken for synthesis of the salt. To a solution of the acid in acetone there was added anabasine. The white flakes which precipitated out at first converted to a white powder when stirred with a rod. The compound was so hygroscopic that upon filtration by suction, and repeated washing with acetone in a special apparatus, it melted rapidly. Analysis for the acid content only was carried out, because of the extreme hygroscopicity of the salt. Several batches were taken for analysis, and each time a sample was taken from a freshly synthesized portion of salt.

Found %: H_3PO_4 16.96, 16.31. $3C_{10}H_{14}N_2 \cdot H_3PO_4$. Calculated %: H_3PO_4 16.76.

Data given in the present and in the preceding [1] articles indicate that monobasic inorganic acids form compounds with anabasine which are stable in air. They are all electrolytes and possess considerable electroconductivity. Anabasine sulfate and phosphate salts are highly hygroscopic. The examples considered also indicate that anabasine behaves predominately as a monoacidic base during interaction with inorganic acids, which leads to formation of the crystalline compound.

SUMMARY

1. A crystalline salt of anabasine with hydrogen bromide has been obtained, of the composition $C_{10}H_{15}N_2 \cdot HBr$.

2. A crystalline salt of anabasine with hydrogeniodide, of the composition $C_{10}H_{14}N_2 \cdot HI$ has been synthesized.

3. A solid hygroscopic salt of anabasine with sulfuric acid, of the composition $C_{10}H_{14}N_2 \cdot H_2SO_4$ has been synthesized.

4. A solid hygroscopic salt of anabasine with orthophosphoric acid, of the composition $3C_{10}H_{14}N_2 \cdot H_3PO_4$ has been obtained.

5. It has been demonstrated that anabasine, as crystalline salts with inorganic acids, behaves predominately as a monoacidic base.

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* See Consultants Bureau Translation, page 955.

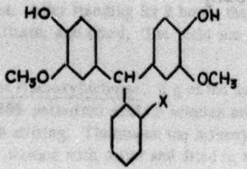
RESEARCH IN THE FIELD OF HYDROXYFUCHSONE DYES

XVIII. HALOGEN DERIVATIVES OF 3,3'-DIMETHOXYBENZAURIN

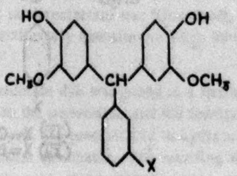
I. S. Ioffe and B. G. Belenky

Extending the work described in the preceding article [1], the authors have obtained halogen derivatives of 3,3'-dimethoxy-4'-hydroxyfuchsone, containing chlorine and bromine atoms in different positions of the phenyl ring.

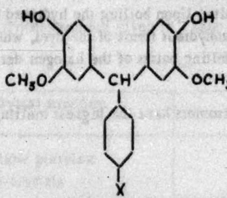
The corresponding leuco derivatives (I–VI) were obtained by condensing isomeric chlorobenzaldehydes and bromobenzaldehydes with guaiacol in the presence of hydrogen chloride.



(I) X=Cl
(IV) X=Br



(II) X=Cl
(V) X=Br



(III) X=Cl
(VI) X=Br

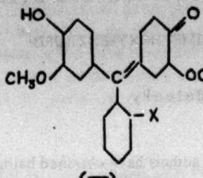
All of these triphenylmethane derivatives were obtained, after crystallization from alcohol or from acetic acid, in the form of colorless crystals, whose melting points are given in Table 1.

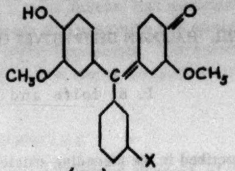
TABLE 1

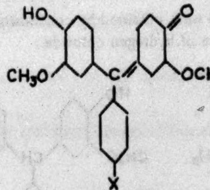
No.	Name of compound		Melting point (in °C)
I	2''-Chloro-	3,3'-dimethoxy-4,4'-dihydroxytriphenylmethane	120-130 (with decomposition)
II	3''-Chloro-		130-140 (with decomposition)
III	4''-Chloro		129-130
IV	2''-Bromo-		120-130 (with decomposition)
V	3''-Bromo-		120-130 (with decomposition)
VI	4''-Bromo-		126-127

It should be stressed that o- and m-halogen derivatives are unstable when heated above 100°, and are subject to some conversions that have not been studied up to the present time; the p-derivative , however, melted sharply within a 1° range.

By passing nitrogen oxides through solutions of all leuco derivatives, in amyl acetate saturated with hydrogen chloride, the authors obtained salts of the corresponding hydroxyfuchsone dyes (VII-XII):


(VII) X = Cl
(X) X = Br


(VIII) X = Cl
(XI) X = Br


(IX) X = Cl
(XII) X = Br

These salts were hydrolyzed by water, converted into the hydrated forms of hydroxyfuchsones. Hydrolysis was more rapid in the presence of acetic acid salts. Upon boiling the hydrated forms with acetic acid, and distilling off the solvent in vacuo, there resulted the anhydrous forms of the dyes, which were purified by crystallization from dry benzene or from glacial acetic acid. Melting points of the halogen derivatives of 3,3'-dimethoxy-4'-hydroxyfuchsone are given in Table 2.

As can be seen from this work, the p-isomers have the highest melting points, and the m-isomers give the lowest.

TABLE 2

No.	Substance name		Melting point (in °C)
VII	2''-Chloro-	3,3'-dimethoxy-4-hydroxyfuchsone	164-166
VIII	3''-Chloro-		147-148
IX	4''-Chloro-		203
X	2''-Bromo		171-172
XI	3''-Bromo		143-144
XII	4''-Bromo		202-205

EXPERIMENTAL

I. Leuco Derivatives of the Dyes

0.05 mole of the aldehyde (7 g of chlorobenzaldehyde or 9.25 g of bromobenzaldehyde) was dissolved in a thick-walled beaker with 0.12 mole of molten guaiacol (15 g) and a stream of dry hydrogen chloride passed through the resulting mixture to saturation. After standing for one week in a hermetically-sealed vessel, the mixture solidified to a homogeneous crystalline monolith. The crude reaction product was treated with hot water and it then melted. After this procedure, the substance was heated several times with 100 ml of 10% soda solution until it became solid in boiling water. The yield of product purified in such fashion was faintly colored, gray-green in color, and varied in yield for individual leuco derivatives from 65-80% of theory. Such product was in itself suitable for further oxidation to the hydroxyfuchsone dye.

To obtain the lueco derivative in analytically-pure form, the product described above was flushed with a small volume of alcohol, which dissolved the impurities, and after filtration, the product was crystallized several times from alcohol or acetic acid.

Halogen was determined on the resulting compound (according to Stepanov). The analytical results are given in Table 3.

TABLE 3

No.	Formula	Batch (in g)	0.1 N $AgNO_3$* (in ml)	Halogen found (in %)	Halogen calculated (in %)
I	$C_{21}H_{19}O_4Cl$	0.2033, 0.2113	5.30, 5.55	9.25, 9.31	9.58
II	$C_{21}H_{19}O_4Cl$	0.2040, 0.1980	5.43, 5.30	9.45, 9.48	9.58
III	$C_{21}H_{19}O_4Cl$	0.2132, 0.2240	5.78, 5.95	9.62, 9.43	9.58
IV	$C_{21}H_{19}O_4Br$	0.2430, 0.2445	5.78, 5.90	19.00, 19.30	19.27
V	$C_{21}H_{19}O_4Br$	0.2135, 0.2110	5.15, 5.05	19.30, 19.13	19.27
VI	$C_{21}H_{19}O_4Br$	0.1998, 0.2018	4.75, 4.85	19.00, 19.21	19.27

II. Hydroxyfuchsone Dyes

A. Synthesis of the Dye Hydrochlorides. 5 g of the leuco derivative (crude condensation product washed free of guaiacol excess can be taken for the reaction) was dissolved in 50 ml of amyl acetate; the resulting solution was saturated with dry hydrogen chloride, and then, along with hydrogen chloride, a stream of nitrogen oxides containing nitrogen dioxide was passed in for 2 hours. Thereupon the dye hydrochloride formed a precipitate in the form of bronze flakes. After standing for 2 hours, the dye salt precipitate was filtered off, washed with amyl acetate to a colorless filtrate, and dried. The yield was approximately quantitative when pure leuco compound was used.

B. Synthesis of Hydroxyfuchsone. 5 g of the hydrochloride dye was gound in a mortar with 50 ml of acetic acid, and 50 ml of 25% potassium acetate solution added to the suspension, and the resulting mixture poured into 250 ml of water with stirring. Thereupon the hydroxyfuchsone dye precipitated in hydrated form as brick-red flakes, which were filtered, washed with water and dried in a vacuum desiccator. The resulting substance was dissolved with heating in 50 ml of glacial acetic acid, and the acetic acid, along with the water which separated from the hydrated form, was distilled off from the solution in vacuo. Ether was poured over the precipitate, filtered, dried in a desiccator. The resulting substance crystallized nicely from dry benzene or glacial acetic acid.

Properties of the hydroxyfuchsone synthesized are given in Table 4.

TABLE 4

No.	Halogen position	Crystal structure	Color of solution	
			in the acid	in alkali
VII	o-Cl	Orange-yellow platelets	Dark-purple	Blue-violet
VIII	m-Cl	Orange-red crystals	Violet	Blue
IX	p-Cl	Red prisms	Purple-red	Blue
X	o-Br	Yellow-orange platelets	Violet	Blue-violet
XI	m-Br	Red crystals	Purple	Blue-violet
XII	p-Br	Red crystals	Purple	Blue

For the dyes synthesized, halogen was determined according to Stepanov. Analytical data are given in Table 5.

TABLE 5

No.	Formula	Batch (in g)	0.1 N $AgNO_3$* (in ml)	Halogen found (in %)	Halogen calculated (in %)
VII	$C_{21}H_{17}O_4Cl$	0.2100, 0.2054	5.58 5.33	9.43, 9.22	9.64
VIII	$C_{21}H_{17}O_4Cl$	0.2213, 0.2210	5.85, 5.90	9.36, 9.49	9.64
IX	$C_{21}H_{17}O_4Cl$	0.1988, 0.1930	5.38, 5.23	9.61, 9.62	9.64
X	$C_{21}H_{17}O_4Br$	0.2045, 0.2130	4.88, 5.10	19.10, 19.15	19.35
XI	$C_{21}H_{17}O_4Br$	0.2320, 0.2450	5.53, 5.83	19.06, 19.03	19.35
XII	$C_{21}H_{17}O_4Br$	0.2240, 0.2276	5.33, 5.43	19.03, 19.10	19.35

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* Quantity of $AgNO_3$ used for tying up halogen.

SUMMARY

By condensing isomeric chlorobenzaldehydes and bromobenzaldehydes with guaiacol, the corresponding triphenylmethane derivatives have been obtained, from which, by oxidation with nitrogen oxides in amyl acetate saturated with hydrogen chloride, the hydrochloride salts of the isomeric chloro- and bromo-derivatives of 3,3'-dimethoxy-4'-hydroxyfuchsone have been obtained. The free hydroxyfuchsone dyes have been obtained in analytically-pure form from the salts.

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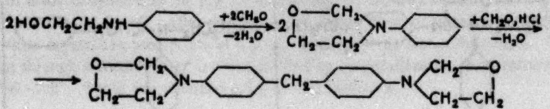
* See Consultants Bureau Translation, page 1597.

INTERACTION OF 3-PHENYLOXAZOLIDINE AND SOME OTHER OXAZILIDINE DERIVATIVES WITH FORMALDEHYDE

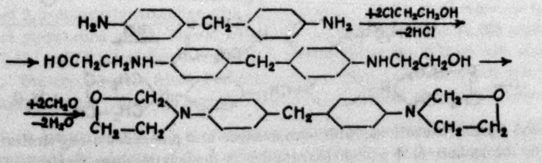
K. D. Petrov and O. K. Gosteva

The authors described earlier [1] the reaction of 3-phenyloxazolidine with formaldehyde, which takes place in the presence of hydrochloric acid, forming p,p'-di(oxazolidyl-3)-diphenylmethane. As new observations have indicated, it is more expedient to synthesize the same product from ethanolaniline and formaldehyde in alcoholic medium. The process in this case is carried out in such a manner that the 3-phenyloxazolidine (in the form of an oil layer) which is forming from the ethanolaniline and formaldehyde is dissolved by addition of alcohol, and condensed further with formaldehyde in the presence of hydrochloric acid to give p,p'-di(oxazolidyl-3)-diphenylmethane:



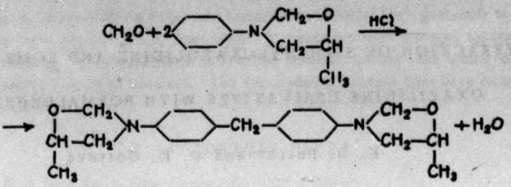
In this case the product resulted in purer form in about 80% yield. Its structure is conditioned by its mode of formation. It is generally known that N-alkylanilines condense with formaldehyde at the p-position, with formation of the corresponding diphenylmethane derivatives [2]. However, 3-phenyloxazolidine having in its structure the $-CH_2-\underset{|}{N}-CH_2-$, arrangement of atoms, is structurally close to that of N-alkylanilines. Hence its reaction with formaldehyde probably proceeds at the p-position, i.e., with formation of p,p'-di(oxazolidyl-3)diphenylmethane.

Moreover, the structure of p,p'-di(oxazolidyl-3)-diphenylmethane is confirmed by its synthesis from p,p'-diaminodiphenylmethane:



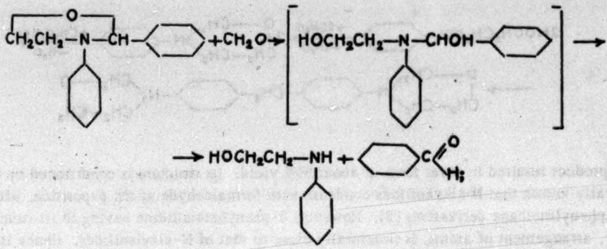
While carrying out this synthesis, p,p'-diethanoldiaminidiphenylmethane (intermediate product) failed to separate in the pure state due to the presence of resinous side-products in the reaction mixture. Therefore, in order to obtain the p,p'-di-(oxazolidyl-3)-diphenylmethane, the authors used crude p,p'-diethanoldiaminodiphenylmethane. For this purpose, the latter was mixed with formaldehyde and heated. The p,p'-di-(oxazolidyl-3)diphenylmethane melted at 141-142°, i.e., in the same range as the condensation product of 3-phenyloxazolidine with formaldehyde (m.p. 141-142°). A mixed sample also melted at 141-142°. Thus was confirmed the identity of these substances, and hence also the fact that reaction of 3-phenyloxazolidine with formaldehyde actually does proceed with formation of p,p'-di-(oxazolidyl-3)-diphenylmethane.

Apart from the above, the formaldehyde reaction with 3-phenyl-5-methyloxazolidine with 2,3-diphenyloxazolidine, and with 2-furyl-3-phenyloxazolidine, was also studied. Here reaction of 3-phenyl-5-methyloxazolidine with formaldehyde proceeded with formation of p,p'-di-(5-methyloxazolidyl-3)-diphenylmethane:

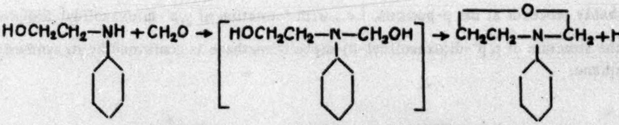


This was confirmed by analysis of the product obtained, and by determination of its molecular weight.

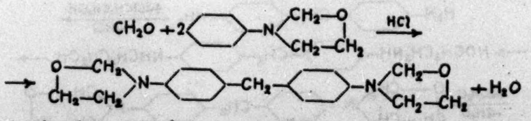
However, reaction of 2,3-diphenyloxazolidine and of 2-furyl-3-phenyloxazolidine with formaldehyde proceeds in another direction. Thus, for example, the reaction of 37% formalin with 2,3-diphenyloxazolidine in the presence of hydrochloric acid gave benzaldehyde and p,p'-(oxazolidyl-3-)diphenylmethane, instead of the expected p,p'-di-(2-phenyloxazolidyl-3)diphenylmethane. Formation of these compounds can be explained as follows:



(1)



(2)



(3)

Reaction of 2-furyl-3-phenyloxazolidine* with formaldehyde also proceeded along similar lines. When this reaction was carried out by the authors, only p,p'-di-(oxazolidyl-3)-diphenylmethane resulted. Furfural failed to separate from the reaction mass because of its resinification.

EXPERIMENTAL

(V. I. Pukhova participating)

1. Synthesis of p,p'-Di-(oxazolidyl-3)-diphenylmethane from Ethanolaniline and Formaldehyde. 3-Phenyloxazolidine was first prepared from ethanolaniline and formaldehyde by gradual addition of 411 g (3 moles) of ethanolaniline to 439 g of 36.9% formalin (5.4 moles CH_2O). The process was carried out with stirring, accompanied by spontaneous evolution of heat and formation of an oily layer of 3-phenyloxazolidine, which settled to the bottom of the container. After addition of all of the ethanolaniline, alcohol was added to the reaction mixture to the formation of a homogeneous, transparent solution – 950 ml. Then, 9 ml of hydrochloric acid (d 1.18) was added, with

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* Synthesis of initial 2-furyl-3-phenyloxazolidine for carrying out this reaction is described in the experimental part. At the same time is also given synthesis for 2-furyl-3-phenyl-5-methyloxazolidine.

stirring, to the mixture. The resulting p,p'-di-(oxazolidyl-3)-diphenylmethane precipitated in the form of white scales. The crystals were filtered off on a Nutsch filter and dried at 95-100° to constant weight. The yield of p,p'-di-(oxazolidyl-3)-diphenylmethane was 360 g (77.40%). The resulting product melted at 136-137°; after recrystallization from alcohol, it melted in the range 141-142°. A sample mixed with known p,p'-di-(oxazolidyl-3)-diphenylmethane (see experiment 2) also melted at 141-142°. Identity of the resulting product with p,p'-di-(oxazolidyl-3)-diphenylmethane was confirmed by analysis.

0.2302 g sub.: 0.6208 g CO_2; 0.1466 g H_2O. 0.1782 g sub.: 0.4791 g CO_2; 0.1242 g H_2O. Found %: C 73.62, 73.39; H 7.13, 7.12. $C_{19}H_{22}O_2N_2$. Calculated %: C 73.50, H 7.09.

2. Synthesis of p,p'-di-(oxazolidyl-3)-diphenylmethane from diaminodiphenylmethane and ethylene chlorohydrin. The p,p'-diethanoldiaminodiphenylmethane was prepared first by heating on an oil bath 19.8 g (0.01 mole) of diaminodiphenylmethane with 17.7 g (0.22 mole) of ethylene chlorohydrin in the presence of 3 ml of water, according to Shorygin [3, 4]. Reaction was carried out with mechanical stirring. The reaction mixture solidified after 8 hours of heating. 50 ml of alcohol was added in order to dissolve it, and the reaction mass was then heated for another 8 hours. After completion of the process, the resulting product (p,p'-diethanoldiaminodiphenylmethane) was treated with saturated soda solution and was filtered on a Nutsch filter, and the filtrate then diluted with 50 ml of alcohol. The p,p'-diethanoldiaminodiphenylmethane could not be isolated by recrystallization from alcohol.

The alcoholic solution of crude p,p'-diethanoldiaminodiphenylmethane was mixed with 17.8 g of 37% formalin (0.22 mole of CH_2O) in order to synthesize the p,p'-di-(oxazolidyl-3)-diphenylmethane, heating being carried out on a water bath for 15 minutes at 50-60°. After standing for 24 hours, there separated from the reaction mixture at room temperature a white crystalline precipitate of p,p'-di-(oxazolidyl-3)-diphenylmethane. The resulting product was filtered by suction through a Nutsch filter and was purified by recrystallization from benzene, after which procedure it melted at 141-142°. There was obtained 4.6 g of pure substance.

0.3781, 0.7231 g sub.: 24.08, 45.63 ml 0.1 N H_2SO_4. Found %: N 8.91, 8.83, $C_{19}H_{22}O_2N_2$. Calculated %: N 9.03.

3. p,p'-Di-(5-methyloxazolidyl-3)-diphenylmethane. 40.8 g (0.25 mole) of 3-phenyl-5-methyloxazolidine was mixed with 61.4 g of 36.6% formalin (0.74 mole of CH_2O), 10 ml of dioxane, and 2 ml of hydrochloric acid (d 1.18). The reaction was carried out with mechanical stirring for 4 hours. A white crystalline product precipitated. After completion of the process, the reaction mixture was neutralized with soda solution. The crystals were aspirated off onto a Nutsch filter; they melted at 95-96°. 16 g of substance was obtained.

0.2674 g sub.: 0.7266 g CO_2; 0.1910 g H_2O. 0.6418 g sub.: 37.15 ml 0.1 N H_2SO_4. 0.1223 g sub.: 30.82 g of benzene: Δt: 0.06°. Found %: C 74.12; H 7.90; N 8.10; M 339. $C_{21}H_{26}O_2N_2$. Calculated %: C 74.56; H 7.69; N 8.28; M 338.

4. Interaction of 2,3-diphenyloxazolidine with formaldehyde. 11.3 g (0.05 mole) of 2,3-diphenyloxazolidine (concerning which preparation see [3, 5]) was mixed with 8 g of 37% formalin (0.098 mole CH_2O), 1 ml of hydrochloric acid (d 1.18) and 50 ml of dioxane. Reaction was continued for 18 hours with stirring until a white precipitate separated. The crystals were filtered off onto a Nutsch filter and washed with soda solution, followed by water. 5 g of crystals resulted. After two recrystallizations from alcohol, the product melted at 141-142°.

The mixture with a known sample of p,p'-di-(oxazolidyl-3)-diphenylmethane (m.p. 141-142°) melted in the same range, which confirmed the identity of these substances. According to the analytical data, the product resulting from this experiment also corresponded to p,p'-di-(oxazolidyl-3)-diphenylmethane.

0.1682 g sub.: 0.4549 g CO_2; 0.1128 g H_2O. Found %: C 73.73; H 7.50. $C_{19}H_{22}O_2N_2$. Calculated %: C 73.50; H 7.09.

In investigating the filtrate obtained by vacuum filtration of p,p'-di-(oxazolidyl-3)-diphenylmethane, the benzaldehyde failed to separate in sufficiently pure state, and the experiment had to be repeated. For this purpose, 60 g (0.27 mole) of 2,3-diphenyloxazolidine, 43.7 g of 36.6% formalin (0.54 mole CH_2O), 1 ml of hydrochloric acid (d 1.18) and 200 ml of dioxane were taken for reaction. 8.3 g of p,p'-di-(oxazolidyl-3)-diphenylmethane (m.p. 141-142°) was formed, along with 6.9 g of benzaldehyde, and separation of the benzaldehyde was carried out by fractionation of the filtrate after filtering off the p,p'-di-(oxazolidyl-3)-diphenylmethane with suction. Dioxane was first removed on the column at atmospheric pressure, and the residue, with a characteristic odor of benzaldehyde, was distilled from a Claisen flask at decreased pressure. In order to remove impurities from the resulting product it was then distilled for a second time at atmospheric pressure. The benzaldehyde was collected in the range 176-179° at 745 mm. 6.9 g was obtained; $n_D^{19.5}$ 1.5448; d_{20}^{20} 1.0455. Upon subsequent distillation of this fraction the benzaldehyde was collected in a narrower range, 178-179° at 754 mm. 1.8 g resulted; $n_D^{19.5}$ 1.5455. The following constants are given in the literature [6] for benzaldehyde: b.p. 178.3 at 760 mm; 179.1° at 751.3 mm; $n_D^{19.5}$ 1.5456; d_{15}^{15} 1.0500; d_{25}^{25} 1.0434).

The resinous reaction products (distillation residues) which resulted from this experiment were not investigated further by the authors.

5. 2-Furyl-3-phenyloxazolidine was prepared by stirring 96 g (1 mole) of furfural with 137 g (1 mole) of ethanolaniline for 10 minutes in the presence of 1 g of potash, after which the reaction mixture was fractionated in vacuo. The 2-furyl-3-phenyl-oxazolidine fraction was collected in the range 165-171° at 7 mm. 137 g of substance resulted. Yield was 63.39% of theory. The resulting product externally resembled a yellow oil (darkening during a lapse of time):

d_{20}^{20} 1.1781; n_D^{20} 1.5855; MR_D 61.40; calculated 60.53.

0.3980 g sub.: 1.0594 g CO_2; 0.2270 g H_2O. 1.7724 g sub.: 25.54 g benzene: Δt 1.625°. Found %: C 72.60; H 6.38; M 219. $C_{13}H_{13}O_2N$. Calculated %: C 72.55; H 6.04; M 215.

6. 2-Furyl-3-phenyl-5-methyloxazolidine. 151 g (1 mole) of β-hydroxypropylaniline was mixed with 105.68 g (1.1 moles) of freshly distilled furfural and 2 g of potash. The mixture was further distilled in vacuo. The 2-furyl-3-phenyl-5-methyloxazolidine fraction was collected in the range 130-135° at 1.5 mm. There resulted 165 g (72%) of substance. The product superficially resembled a thick, viscous, yellowish oil (darkening with time).

d_{20}^{20} 1.1334; n_D^{20} 1.5710; MR_D 66.07; calculated 65.14.

0.4382 g sub.: 1.1788 g CO_2; 0.2722 g H_2O. 0.7928 g sub.: 28.06 g benzene: Δt 0.63°. Found %: C 73.37; H 6.90; M 230. $C_{14}H_{15}O_2N$. Calculated %: C 73.36; H 6.35; M 229.

7. Interaction of 2-furyl-3-phenyloxazolidine with formaldehyde. 18.5 g (0.086 mole) of 2-furyl-3-phenyloxazolidine was mixed with 14 g of 37% formalin (0.172 mole CH_2O), 100 ml of alcohol and 0.5 ml of strong hydrochloric acid. Reaction was carried out for 18 hours, and processed as in the preceding case (see experiment 4), with formation of p,p'-di-(oxazolidyl-3)-diphenylmethane. After recrystallization from alcohol, 12 g of product with m.p. 141-142° resulted. A sample mixed with known sample of p,p'-di-(oxazolidyl-3)-diphenylmethane (see experiment 2) melted at the same temperature, indicating identity of these substances. The resinous reaction products obtained in this experiment were not investigated further.

SUMMARY

1. A method for synthesis of p,p'-di-(oxazolidyl-3)-diphenylmethane has been described.

2. Synthesis of p,p'-di-(5-methyloxazolidyl-3)-diphenylmethane, 2-furyl-3-phenyl-oxazolidine and 2-furyl-3-phenyl-5-methyloxazolidine, not described in the literature, has been given.

3. It has been established that, contrary to expectations, 2,3-diphenyloxazolidine reacts with formaldehyde to form p,p'-di-(oxazolidyl-3)-diphenylmethane and benzaldehyde. A reaction mechanism for this reaction has been given. It has been established that according to similar scheme 2-furyl-3-phenyloxazolidine reacts with formaldehyde.

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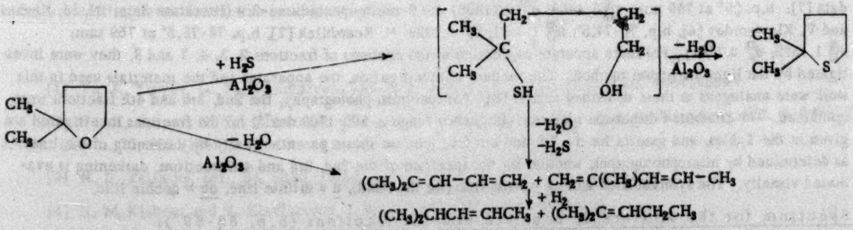
CATALYTIC CONVERSION OF 2,2-DIMETHYLFURANIDINE INTO 2,2-DIMETHYLTHIOPHANE AND INTO HYDROCARBONS. XLI.

Yu. K. Yuryev, G. Ya. Kondratyeva and P. A. Akishin

It was pointed out in the preceding article [1] that the principal factors which limit completeness of the conversion of furanidine homologs to the corresponding thiophane homologs are the number and types of alkyl groups bound to the furanidine ring, as well as their positions relative to the oxygen bridge of this ring. Whereas furanidine converts almost completely into thiophane, and 3,3-dimethylfuranidine into 3,3-dimethylthiophane [1], in yields (73%) approximating that for 3-methylthiophane as obtained from 3-methylfuranidine, the reaction of 2,2,5,5-tetraalkylfuranidines with hydrogen sulfide under catalytic conditions for conversion of heterocycles produce only mixtures of two unsaturated hydrocarbons with different double bond locations [2]. The formation of diene hydrocarbons in this case is conditioned by the simultaneous splitting out of water and hydrogen sulfide from the intermediate ditertiary 1,4-mercaptohydroxy compounds.

In its structure, 2,2-dimethylfuranidine lies between furanidine and 2,2,5,5-tetramethylfuranidine. It should, by adding hydrogen sulfide under the conditions of catalytic conversion of heterocycles, convert into the intermediate, primary, tertiary mercaptohydroxy compound $(CH_3)_2C(SH)CH_2CH_2CH_2OH$, which should be able to split out water and hydrogen sulfide to form the diene hydrocarbon, and to split out water, forming only the cyclic compound, 2,2-dimethylthiophane.

It has been determined in the present work that 2,2-dimethylfuranidine, when passed over aluminum oxide in a stream of hydrogen sulfide at 350°, does in fact produce 2,2-dimethylthiophane (yield 27%) and a mixture of unsaturated hydrocarbons. Catalytic dehydration of 2,2-dimethylfuranidine in the absence of hydrogen sulfide led to the formation of a hydrocarbon mixture which contained 2-methylpentadiene-1,3, 2-methylpentadiene-2,4, 2-methylpentene-2 and 2-methylpentene-3.



Formation of ethylenic hydrocarbons is explained by reduction of diene hydrocarbons with hydrogen which appears in the reaction zone as the result of destructive processes.

EXPERIMENTAL

2,2-Dimethylfuranidine. Acetopropyl alcohol (25 g) was added to an ether solution of methylmagnesium iodide (from 12 g of Mg and 75 g of CH_3I in 250 ml of absolute ether) with cooling and stirring. After completion of the violent reaction, the mixture was stirred at room temperature for 1 hour, and was then decomposed with 170 g of ice and 20 ml of concentrated H_2SO_4. The resulting oxide was distilled with steam and 200 ml of distillate collected. The distillate was saturated with sodium chloride, the light upper layer which rose to the top separated, and the aqueous solution extracted 3 times with ether. The ether extracts were combined with the main oxide and dried over calcium chloride. After distilling off the ether, followed by two distillations of the residue over sodium, there resulted 13.5 g of 2,2-dimethylfuranidine (54% of theory); b.p. 92.2-92.4° (758 mm); n_D^{20} 1.4045; d_4^{20} 0.8441; MR_D 29.05, $C_6H_{12}O$. Calculated: MR_D 29.35.

Literature data: N. D. Zelinsky [3], b.p. 92-93° (746 mm); n_D^{21} 1.4063; d_4^{21} 0.8350; N. M. Kizhner and V. Klavikordov [4], b.p. 92.5-92.7° (764 mm); n_D^{20} 1.4075; d_0^{20} 0.8394.

Conversion of 2,2-dimethylfuranidine to 2,2-dimethylthiophane. 45 g of 2,2-dimethylfuranidine was passed over aluminum oxide at 350° at a rate of 0.6 ml/min. in a stream of hydrogen sulfide. The catalyzate was saturated with sodium hydroxide, the oily layer separated and dried over sodium hydroxide, followed by distillation. Upon distillation, the following fractions separated: 1st with b.p. 35-55°, 1.1 g; 2nd with b.p. 55-70°, 3.2 g; 3rd with b.p. 70-135°, 2 g; 4th with b.p. 135-142°, 16.2 g; 5th with b.p. 142-200°, 5.2 g; and a residue of 7.3 g, a viscous, semi-transparent mass. Fractions 1, 2 and 3 contained unsaturated compounds, but did not contain sulfur compounds. From the 4th fraction, after two distillations, 14.2 g of 2,2-dimethylthiophane (27% of theory) resulted: b.p. 138-138.8° (750 mm); n_D^{20} 1.4807; d_4^{20} 0.9220; MR_D 35.85. $C_6H_{12}S$. Calculated 35.68. The melting point of the compound with $HgCl_2$ was 131-133°. The 2,2-dimethylthiophane has not been described in the literature.

8.270 mg sub.: 18.800 mg CO_2; 7.480 mg H_2O; 6.730 mg SO_4. 7.750 mg sub.: 17.630 mg CO_2; 7.050 mg H_2O; 6.440 mg SO_4. Found %: C 62.03, 62.08; H 10.12, 10.18; S 27.81, 27.75. $C_6H_{12}S$. Calculated %: C 62.00; H 10.41; S 27.59.

Catalytic dehydration of 2,2-dimethylfuranidine. 75 g of 2,2-dimethylfuranidine was passed over aluminum oxide at 350° at a rate of 0.5 ml/min. in a stream of nitrogen. The receiver and the trap into which the catalyzate went, were cooled with an ice-salt mixture. The total weight of catalyzate was 60 g, the weight of the hydrocarbon layer was 46 g. After drying with calcium chloride, the hydrocarbon mixture was distilled (at 756 mm) on a column with an efficiency of 25 theoretical plates.

The following fractions were isolated: 1st, b.p. to 53°, 0.5 g, n_D^{20} 1.3842; 2nd, b.p. 53-57°, 2.0 g, n_D^{20} 1.3850, d_4^{20} 0.6677; 3rd, b.p. 57-60°, 1.0 g, n_D^{20} 1.3915; 4th, b.p. 66-69°, 2.0 g, n_D^{20} 1.4103, d_4^{25} 0.6840; 5th, b.p. 69-72°, 2.0 g, n_D^{20} 1.4207; 6th, b.p. 72-74.5°, 0.4 g, n_D^{20} 1.4360; 7th, b.p. 74.5°, 5.3 g, n_D^{20} 1.4470, d_4^{20} 0.7240; 8th, b.p. 75.4°, 3.0 g, n_D^{20} 1.4495, d_4^{20} 0.7186.

The residue, after cooling, polymerized to a colorless, vitreous mass.

The 2nd fraction, from its constants, corresponded to 2-methylpentene-3 (literature data: A. Gorsky [5], b.p. 57-58.5° at 760 mm; n_D^{20} 1.3883; d_4^{20} 0.6707); the 4th fraction resembled closely, in its boiling range, 2-methylpentene-2, but possessed a higher refractive index, apparently due to the presence of 2-methylpentadiene impurities (literature data of 2-methylpentene-2: C. Schmitt and C. Boord [6], b.p. 67.2-67.5° at 760 mm; n_D^{20} 1.4005; d_4^{20} 0.6904). The 7th and 8th fractions, judging from their constants, contained 2-methylpentadiene-1,3 (literature data [7]: b.p. 76° at 760 mm; n_D^{20} 1.4466; d_4^{20} 0.71896) and 2-methylpentadiene-2,4 (literature data: N. M. Kizhner and V. Klavikordov [4], b.p. 76-77.5°; n_D^{20} 1.4491; d_4^{20} 0.7229; N. Keersbilck [7], b.p. 76-76.5° at 759 mm; n_D^{20} 1.4532; d_4^{20} 0.7181). For more accurate evaluation of the contents of fractions 2, 3, 4, 7 and 8, they were investigated by the light dispersion method. The method of investigation, the apparatus and the materials used in this work were analogous to those described earlier [8]. For spectrum photography, the 2nd, 3rd and 4th fractions were combined. The combined dispersion spectrum (frequency range ω 200-1700 cm^{-1}) for the fractions investigated are given in the Tables, and spectra for the 7th and 8th fractions are shown parenthetically by darkening of the lines as determined by microphotographs, whereas for the spectrum of the 2nd, 3rd and 4th fractions, darkening is evaluated visually. The symbols used are: w = wide line (for the band), d = diffuse line, db = double line.

Spectrum for the Mixture of 2nd, 3rd and 4th fractions (b.p. 53-69°):

ω: **314** (0); **357** (2); **402** (1) d; 447 (1) w; 487 (0); **514** (2) db; 533 (3); **746** (1) w; **813-836** (5) w, db; **886-904** (2) w; 938 (1); 956-967 (1) db; **1014** (5); **1062** (2); 1104 (4); 1149 (2); 1170 (1); 1196 (1); **1217** (2); 1250 (1) d; **1304** (13); 1332 (2); **1359** (1) d; **1382** (10); 1414 (2); 1451 (10) w; 1601 (0); 1612 (4); 1641 (13); **1658** (15); 1678 (13).

The data given makes it possible, by measuring the most intense lines (bold type) [9], to determine quite reliably the presence of 2-methylpentene-2 in a mixture of the 2nd, 3rd and 4th fractions. From a series of lines, chiefly by the characteristic line 1672 cm^{-1} [9], can also be determined the presence of the trans isomer of 2-methylpentene-3. There should be taken into account literature data [9], according to which the spectrum for pure 2-methylpentene-3 was obtained on an apparatus with photoelectric recording with a wide slit (~ 11 cm^{-1}), because of which considerable deviation in frequencies (from 2 to 10 cm^{-1}) is possible.

Spectrum for the 7th Fraction (b.p. 74.5°):

ω: 200 (2) w; 246 (0) w; 306 (0); 363 (7); 436 (4); 447 (7); 476 (1); 495 (1); 526 (2); 535 (12); 587 (0) d; 680 (0) d; 706 (0) d; 770 (0) d; 812 (10); 827 (7); 860 (0); 882 (10) w; 897 (9) w; 935 (3); 960 (2); 992 (1); 1015 (20); 1041 (2); 1070 (2) d; 1103 (8); 1147 (15); 1157 (0) d; 1217 (24); 1246 (1) d; 1270 (8); 1293 (8); 1306 (32); 1332 (21); 1359 (2); 1380 (20); 1414 (14); 1453 (24) w; 1602 (29); 1612 (29); 1640 (20); 1660 (51).

Spectrum for the 8th Fraction (b.p. 75.4°):

ω: 200 (3) w; 362 (8); 437 (6); 447 (6); 480 (1); 495 (1); 524 (3); 535(9); 587 (0)d; 680 (0) d; 702 (0) d; 770 (0) d; 811 (9); 828 (3); 862 (1); 886 (2) d; 897 (10) sh; 935 (0); 964 (0); 1015 (16); 1040 (5); 1)68 (5); 1)89 (3) d; 11)3 (6); 1117 (3) d; 1148 (19); 1160 (5); 1217 (27); 1244 (1); 1268 (5); 1293 (15); 1306 (24); 1332 (24); 1354 (2); 1382 (19); 1415 (12); 1453 (23) w; 1603 (27); 1612 (15); 1640-1658 (47) w.

Darkening of weak lines was visually estimated by comparison with parallel standing lines measured by microphotogram.

The 7th and 8th fractions were mixtures of isomeric diene hydrocarbons with a conjugated double bond system, 2-methylpentadiene-2,4 and 2-methylpentadiene-1,3. Determination of the percent composition of each of these fractions was carried out by internal calibration method. In the fraction spectra, the relationships of intensities of the 1219 and the 1330 cm^{-1} lines to the intensity of the 669 cm^{-1} lines of chloroform added in specified amount, were measured photometrically, and on the basis of data on the line intensity for the spectrum of pure 2-methylpentadiene-2,4 [9], calculation of this hydrocarbon was carried out. It was found that the 7th fraction contained about 65% 2-methylpentadiene-2,4 and the 8th fraction about 80%; the content of 2-methylpentadiene-1,3 was determined by difference, i.e., it constituted 35% of the 7th fraction, and 20% of the 8th fraction. Proof of the presence of methylpentadiene-1,3 in the 7th fraction was also the resulting 2,4-dimethyl-Δ^3-tetrahydrophthalic acid. The 7th fraction in dioxane solution was treated with maleic anhydride in the presence of a small amount of hydroquinone [10]. After hydrolysis and steam distillation, 2,4-dimethyl-Δ^3-tetrahydrophthalic acid separated, with m.p. 152°. Literature data: G. Bachman and G. Goebel [10]; m.p. 153-154°; R. Ya. Levina and co-workers [11]: m.p. 153°.

6.690 mg sub.: 13.713 mg CO_2; 4.450 mg H_2O. 5.860 mg sub.: 12.001 mg CO_2; 3.800 mg H_2O. Found %: C 55.94, 55.89; H 7.44, 7.26. $C_{10}H_{13}O_4 \cdot H_2O$. Calculated %: C 55.54; H 7.47.

SUMMARY

1. 2,2-Dimethylfuranidine, when passed over aluminum oxide in a stream of hydrogen sulfide at 350°, converts into 2,2-dimethylthiophane, and at the same time unsaturated hydrocarbons are produced.

2. Upon dehydrating 2,2-dimethylfuranidine over aluminum oxide at 350°, there is formed a mixture of hydrocarbons containing diene hydrocarbons with a conjugated double bond system: 2-methylpentadiene-2,4 and 2-methylpentadiene-1,3, as well as the ethylenic hydrocarbons: 2-methylpentene-2 and 2-methylpentene-3. Ethylenic hydrocarbons are found to be products of secondary reaction: the reduction of diene hydrocarbons with hydrogen resulting from destructive processes.

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ELECTROLYTIC DISSOCIATION IN ANHYDROUS SYSTEMS

I. STANNIC CHLORIDE-ETHYL ACETATE

S. P. Miskidzhyan

Numerous complex compounds found by physico-chemical methods of analysis in various bi-component systems have been defined in the general form, nA · mB, owing to a lack of data regarding their structures. As examples, such known complex compounds as $C_3H_5CNS \cdot C_5H_{10}NH$; $C_6H_5NH_2 \cdot 2CH_3COOH$ and many other molecular compounds discovered by Academician N. S. Kurnakov and his students, can be cited.

Of special interest are those instances of complex formation wherein the components from which the complex compound is formed are non-electrolytes, while the complex compound resulting from them is a good conductor of the electric current. The above-mentioned compounds can be referred to as examples. Thus, the specific electroconductivity isotherm for the aniline-acetic acid system, studied for the first time by D. P. Konovalov [1], possesses a sharply-pronounced maximum, corresponding to the composition of the compound formed in the system. In like manner, corrected electroconductivity diagrams for such systems as allyl mustard oil-piperidine, and others, can be mentioned, from which it can be determined that the complex compound forming in the system is an electrolyte.

A clarification of the type of electroconductivity of similar complex compounds is of interest since it permits a clarification not only of the mechanism of electrolytic dissociation for these compounds, but also because it permits determination, to some degree, of the structures of these complexes, since, up to the present time, there can be found no data on the structures for a majority of the compounds in question.

A study of the electrolytic dissociation in anhydrous systems is also of considerable practical value for a clarification of the mechanisms of electrochemical processes for the industrial synthesis of a variety of products by electrolysis in organic solvents.

The author has selected stannic chloride-ethyl acetate, the viscosity of which and the electroconductivity of which have been studied by N. S. Kurnakov and E. B. Shternina [2]. According to these investigations, the system forms a complex compound of the composition $SnCl_4 \cdot 2CH_3COOC_2H_5$. Formation of such a compound is indicated by a sharply-defined maximum on the viscosity isotherms, the heats of combination, and the minimum on the electroconductivity diagram for this system [3, 4]. If one neglects the viscosity effect, then there will result on the electroconductivity diagram a maximum at approximately the composition of the compound, i.e., at 33.3 mole % stannic chloride, indicated by a high electroconductivity for the chemical compound formed in the system. As is known, none of the components of this system will conduct the electric current. Thus, for example, the specific electroconductivity for ethyl acetate and stannic chloride is $\kappa < 10^{-9}\Omega^{-1}cm^{-1}$. It seemed to the author, therefore, that a study of the electrolytic dissociation mechanism and the nature of the conductivity of the compound could lead to a determination of a structure for the complex.

EXPERIMENTAL

To study the nature of conductivity of the electric current, electrolysis of the above-indicated complex compound was carried out with various mixtures of this system, followed by investigation of the composition and some of the physical properties of the liquid areas around the anode and the cathode, before and after electrolysis.

Electrolysis was carried out in an H-shaped vessel with platinum electrodes, where the cathode space was separated from the anode. A lamp rectifier with terminal voltage of 300 V served for the current source. To measure the amount of electricity, a copper coulometer was switched into the circuit. The current strength fluctuated from 2 to 5 mA at the start of the experiment, and from 15 to 20 mA at the end. Duration of experiments lasted from 8 to 48 hours. Temperature varied from 16 to 19°.

Chemical analysis of the composition of the mixture and of liquid in the anodic and cathodic areas after the electrolysis was carried out as follows. The quantity of tetravalent tin was determined by precipitating it in the form of hydroxide, and subsequent calcining to SnO_2 [5]. The quantity of ethyl acetate in the run was calculated by weight difference in tin tetrachloride for the run. A preliminary control determination indicated that the presence of ethyl acetate does not interfere with tin determination. Tin tetrachloride was obtained by passing chlorine through chemically-pure tin foil [6]. The resulting tin tetrachloride was distilled. The fraction boiling at 112-114° was taken for the work. Density of the preparation obtained at 0° was 2.276. To prepare the second component, the author used ready-prepared, chemically-pure ethyl acetate, which had been kept over anhydrous sodium acetate and sodium carbonate for several days, and distilled with precautionary measure against access of moisture. The fraction boiling at 76-77.5° was collected. Density of the distilled ethyl acetate was 0.9002 at 20°, and the refractive index at the same temperature was 1.3722.

Two initial mixtures were prepared for the investigation: first, from 20 mole % tin tetrachloride and 80 mole % ethyl acetate, and the second mixture of 60 mole % tin tetrachloride and 40 mole % ethyl acetate. A mixture of such composition was taken because such ratios of components corresponded to the maximum electroconductivity for this system.

Preparation of these mixtures was carried out in an H-shaped vessel, as was done by N. S. Kurnakov [3]. In such a vessel gradual mixing of the components, and of cooling, is assured, since otherwise the mixture evolves heat spontaneously due to the heat of chemical reaction, and leads to a partial resinification.

Electrolytic data are given in Table 1 for various mixtures of the system studied by the author, along with the analytical results of liquids at the anodic and cathodic areas, after electrolysis.

TABLE 1

Expt. No.	$SnCl_4$ content in the mixture before electrolysis (in weight %)	$SnCl_4$ content after electrolysis (in %)				Amount of electrolyte passed through the solution (in coulombs)
		in liquid of the anode space	change	in liquid of the cathode space	change	
1	46.91	50.11	+3.60	–	–	318
2	39.10	50.56	+11.46	27.13	−11.97	753
3	39.10	44.76	+5.66	28.41	−10.79	676
4	44.23	48.41	+4.18	38.26	− 5.97	520
5	80.77	84.50	+3.73	80.31	− 0.46	250

There is given in the second column of the Table the composition of the initial mixtures found on the basis of chemical analysis.

The following phenomena were observed during electrolysis:

1) directly following switch-on of the current, accumulation of a gray precipitate of metallic tin occurred at the cathode;

2) at the completion of electrolysis, current increased markedly, due to heating of the liquid at the expense of Joules of heat at the cathode, at which a white precipitate separated, which, by chemical analysis, proved to be $SnCl_2$;

3) evolution of gas bubbles was not observed at the anode; some evolution of gas bubbles was observed at the cathode at the end of an experiment in some cases (when electrolysis had been continued for a long time).

On the basis of Table 1 data, and observations during electrolysis, the following assumptions can be made with regard to the mechanism of electrolytic dissociation of the complex compound in the system, and with regard to the electrochemical processes occurring at the anode and cathode during electrolysis.

1. Apparently, molecules of the complex compound in the system are associated, and are in the form of $(SnCl_4 \cdot 2CH_3COOC_2H_5)_n$. This is indicated by the presence of a sharp maximum on the viscosity isotherm for this system, which occurs at a composition of 1:2, i.e., at the composition of the complex compound forming in the system. On the other hand, the viscosity of the complex compound exceeds by about 250-fold the viscosity of the most viscous of the components, which, in all probability, is related to an association phenomenon for the complex compound molecules. A. N. Sakhanov [7] pointed out formation of associated complex compounds in current-conducting systems.

2. If the presence of association of complex compound molecules is assumed to be possible for the system, then the main process of electrolytic dissociation can be represented in the following manner:

$$(SnCl_4 \cdot 2CH_3COOC_2H_5)_2 \rightleftharpoons [Sn(CH_3COOC_2H_5)_4Cl_2]^{++} + [SnCl_6]^{--}$$

In this case we take the position that aggregated molecules with a high number, $\underline{n}$, break down into smaller aggregates, where $\underline{n} = 2$.

Along with this main process, there apparently proceeds, although on a small scale, a further electrolytic dissociation of the cation according to the following scheme:

$$[Sn(CH_3COOC_2H_5)_4Cl_2]^{++} + SnCl_4 \rightleftharpoons [Sn(CH_3COOC_2H_5)_4]^{++++} + [SnCl_6]^{--}]$$

3. With electrolysis at the electrodes, the following electrochemical processes apparently take place.

At the cathode. At the start of electrolysis, when the ions obtained at the expense of the second dissociation stage are sufficient in number, metallic tin separates at the cathode according to the following reaction:

$$[Sn(CH_3COOC_2H_5)_4]^{++++} + 4e \rightarrow Sn + 4CH_3COOC_2H_5.$$

At high current densities, when there is a shortage of tin ions due to the small rate of electrolytic dissociation of the second stage, $SnCl_2$ separates at the cathode according to the following reaction:

$$[Sn(CH_3COOC_2H_5)_4Cl_2]^{++} + 2e \rightarrow 4CH_3COOC_2H_5 + SnCl_2.$$

The following facts serve to confirm the indicated processes:

a) Separation of metallic tin at the cathode.

b) Separation of $SnCl_2$ as a white precipitate at the cathode; the phenomenon of simultaneous separation of the metal and the salt of the metal at the cathode is known in the literature. Thus, for example, Watkins and Denham [8] indicated the fact that upon electrolysis of aqueous or alcoholic solutions of cupric chloride or bromide, the precipitates were composed of a heterogeneous mixture of copper with copper halide, where the quantity of halide was greater in proportion as the current density was greater. Gore [9], electrolyzing a hydrochloride solution of antimony trichloride, found up to 5% $SbCl_3$ in the metallic precipitate of antimony.

c) The increase in percentage composition of ethyl acetate in the liquid of the cathode space after electrolysis, occurs because of a break-down of the complex ions

$$[Sn(CH_3COOC_2H_5)_4]^{++++} \text{ and } [Sn(CH_3COOC_2H_5)_4Cl_2]^{++}$$

during their discharge at the cathode.

At the anode. The anion discharge apparently proceeds as follows:

$$[SnCl_6]^{--} \rightarrow SnCl_4 + 2Cl + 2e.$$

Atomic chlorine at the moment of evolution enters into reaction with a molecule of ethyl acetate and chlorinates the methyl group:

$$CH_3COOC_2H_5 + 2Cl \rightarrow CH_2ClCOOC_2H_5 + HCl.$$

This assumption appears more probable if there be taken into consideration the literature data [10] with the fact that $SnCl_4$ is found to be a catalyst for chlorination of certain organic compounds. The hydrogen chloride evolved during chlorination interacts with $SnCl_4$ forming

$$2HCl + SnCl_4 \rightleftharpoons H_2SnCl_6.$$

This compound, and perhaps HCl also, has apparently accumulated by the end of the experiment in adequate amount for self-electrolysis to take place according to the reaction:

$$H_2SnCl_6 \rightleftharpoons 2H^+ + SnCl_6^{--}$$

or

$$HCl \rightleftharpoons H^+ + Cl^-,$$

by which time the evolution of gas bubbles at the cathode is limited.

As proof of the fact that the above-indicated reaction occurs at the anode, can be cited the following data: a) a noticeable increase in the stannic chloride content for the liquid of the anode space after electrolysis (Table 1); no evolution of gaseous chlorine at the anode, due to reaction with ethyl acetate molecules, as confirmed by the presence in the ether extract of an organic compound having in its composition chloride ion extracted from the aqueous solution of the anodic space liquid (after electrolysis). Chlorine was found by both the Beilstein method, and by reacting the organic substance with metallic sodium, and subsequent identification of chloride ion by use of silver nitrate.

In order to remove doubt that the chlorine could have gotten into the extracted substance from the aqueous medium where $SnCl_4$ and HCl are present in sufficient amounts, an analogous extraction from initial liquid was carried out, i.e., from the mixture before electrolysis; in this case both tests for chloride were negative.

Another proof of HCl formation in the anode space is given by the fact that the chloride ion precipitated with silver nitrate from the anode area liquid (after electrolysis) using the theoretical quantity of silver nitrate dissolved in water, the required amount of silver nitrate is noticeably greater than that required by calculating on the basis of tin tetrachloride content in the mixture. If the quantity of electricity passed through the solution is accounted for, and the amount of HCl taken into account, which could have been formed in this manner, the correspondence is then approximately in accord with the excess silver nitrate used to precipitate the chloride ions.

Electrolysis of the second of the initial mixtures proceeds, on the whole, as with electrolysis of the first mixture. The difference consists in the fact that in this case a gray precipitate separates (metallic tin) to a considerably greater extent than in the first case. This is explained by the fact that with an excess of tin tetrachloride molecules, the second stage of electrolytic dissociation:

$$[Sn(CH_3COOC_2H_5)_4Cl_2]^{++} + SnCl_4 \rightleftharpoons [Sn(CH_3COOC_2H_5)_4]^{++++} + [SnCl_6]^{--}$$

proceeds with considerably greater slowness.

Some additional proofs of the above-given electrochemical processes proceeding at the anode and cathode during electrolysis of mixtures of the system studied by the author were obtained when a number of physico-chemical constants for the initial mixture and for the anode and cathode area liquids after electrolysis were determined.

In Table 2 there are given the density and apparent molecular weights for the liquids of the anode and cathode area before and after electrolysis.

It can be seen from data given in this table that the density for the mixture in the anode area after electrolysis increases, and decreases in the cathode area. This is in agreement with a clarification of the electrode processes given above. An increase in density of the anode area liquid is caused by the increase in percent content of tin chloride after electrolysis, the density of which is approximately 2-fold greater than the density of the initial mixture.

TABLE 2

Content of $SnCl_4$ in the mixture (weight %)	Density d^{25}			Apparent molecular weight, M			Amount of electricity passed (in coulombs)
	before electrolysis	after electrolysis		before electrolysis	after electrolysis		
		anode area	cathode area		anode area	cathode area	
44.23	1.3470	1.4654	1.2526	281.5	511.4	224.5	520
80.77	1.8570	1.8789	1.8121	334.8	479.4	332.5	250

Decrease in density of the cathode area liquid is related to the increase in percent content of ethyl acetate after electrolysis as a result of the discharge of complex cations. With regard to the apparent molecular weight (measured cryoscopically in benzene solvent), here again, the sharp increase in apparent molecular weight of anode area liquid after electrolysis is explainable by the fact that the $SnCl_6^{--}$ ions, being discharged at the anode, form an additional amount of tin tetrachloride. The latter, by entering into combination with ethyl acetate which is present in excess (in the case of the 20 mole % stannic chloride mixture) forms new molecules of the complex compound $(SnCl_4 \cdot 2CH_3COOC_2H_5)_n$, the molecular weight of which is much greater than that of the initial mixture.

A noticeable decrease in apparent molecular weight for the cathode area liquid after electrolysis is explainable on the basis that upon destruction of the complex cations $[Sn(CH_3COOC_2H_5)_4]^{++++}$ and $[Sn(CH_3COOC_2H_5)_4Cl_2]^{++}$, the amount of ethyl acetate increases, the molecular weight of which is relatively small.

SUMMARY

1. Electrolysis of a mixture of stannic chloride and ethyl acetate has been carried out.

2. On the basis of data obtained by chemical analysis of liquids at the anode and cathode area, before and after electrolysis, and on the basis of measurements of a series of physico-chemical properties for these liquids, a conclusion has been made concerning the mechanism of dissociation of the complex compound.

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KINETICS OF THE CHLOROSULFONATION REACTION. II.

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There have appeared during the past few years a number of works [1, 2, 3, 4] in which kinetics of the chlorosulfonation process has been discussed to some extent; from the present author's point of view, these authors have proceeded from inaccurate premises regarding the reaction mechanism, because of which they came to erroneous conclusions.

Based upon a specifically-defined concept concerning the mechanism of the chlorosulfonation process earlier discussed [5], the author has analyzed the equation for individual reaction rates and has determined experimentally the kinetic curves for accumulation of sulfonyl chlorides during the reaction of chlorosulfonic acid with acetanilide and carbanilide (diphenylurea).

Consider reaction of an aromatic compound, ArH, with chlorosulfonic acid. For the sake of simplification, let it be assumed that this compound does not possess substituents which can interact with chlorosulfonic acid (for example, benzene), so that interaction leads only to formation of monosulfonic acid and monosulfonyl chloride. Thus, formation of polysulfonic acid derivatives, isomeric compounds, sulfones, and others, which in reality do occur to some extent upon chlorosulfonation of various compounds, is excluded by the author from playing any important role. Equally well excluded is the probability of sulfonic acid formation from the ArH compound and sulfuric acid, inasmuch as it was demonstrated earlier by the author [1] that this process proceeds much slower and does not play an important role in chlorosulfonation.

On the basis of the above, the processes can be represented by four major schemes [5].

$$\mathrm{ArH + ClSO_3H \rightarrow ArSO_3H + HCl}, \tag{1}$$

$$\mathrm{ArH + 2ClSO_3H \rightarrow ArSO_2Cl + HCl + H_2SO_4}, \tag{2}$$

$$\mathrm{ArSO_3H + ClSO_3H \rightarrow ArSO_2Cl + H_2SO_4}, \tag{3}$$

$$\mathrm{ArSO_3H + ClS_3OH \leftarrow ArSO_2Cl + H_2SO_4 \rightarrow ArSO_3H + SO_3 + HCl} \tag{4}$$

We might designate the following for molar concentrations of reacting substances: of aromatic compound, A; of chlorosulfonic acid, B; of sulfuric acid, C; the degree of sulfonation (or chlorosulfonation) of the ArH compound, by the variable X, at a given moment of time; and the ratio of molar concentration of sulfonic acid to the concentration of sulfonated products at the moment, t, by the variable Y. The concentration of sulfonic acid will then be expressed as XY, and concentration of sulfonyl chloride as X(1−Y).

If K_1, K_2, K_3 and K_4 are taken as the rate coefficients for the corresponding reactions, then the rate equations for these reactions can be represented as follows (accepting that $K_4 = K_4(\leftarrow) + K_4(\rightarrow)$):

$$\frac{dx_1}{dt} = K_1 \cdot (A-X) \cdot (B-X), \tag{5}$$

$$\frac{dx_2}{dt} = K_2 \cdot (A-X) \cdot (B-2X), \tag{6}$$

$$\frac{dx_3}{dt} = K_3 \cdot XY \cdot [B-X(2-Y)], \tag{7}$$

$$\frac{dx_4}{dt} = K_4 \cdot X(1-Y) \cdot [C+X(1-Y)]. \tag{8}$$

The summated rates for formation of sulfonic acid and sulfonyl chloride will be expressed by the equations:

$$\frac{dx_5}{dt} = K_1(A-X)(B-X) - K_3XY[B-X(2-Y)] + K_4X(1-Y)[C+X(1-Y)],$$

$$\frac{dx_6}{dt} = K_2(A-X)(B-2X) + K_3XY[B-X(2-Y)] - K_4X(1-Y)[C+X(1-Y)].$$

At the moment when X becomes equal to A, i.e., all of the ArH substance has reacted, having become converted to the sulfonic acid, with concentrations AY, and to sulfonyl chloride with A (1−Y) concentration, reactions (1) and (2) cease because

$$\frac{dx_1}{dt} = 0 \text{ and } \frac{dx_2}{dt} = 0.$$

But reactions (3) and (4) will continue, which is the reason why excess chlorosulfonic acid was taken, i.e., if B > 2A, then the rate of formation of sulfonic acid and of sulfonyl chloride will be expressed by the equation:

$$\frac{dx_5}{dt} = -K_3AY[B - A(2-Y)] + K_4A(1-Y) \cdot [C + A(1-Y)],$$

$$\frac{dx_6}{dt} = K_3AY[B - A(2-Y)] - K_4A(1-Y)[C + A(1-Y)],$$

i.e., the latest process occurs in such manner as though it were reversible.

Let us assume that the system is in a state of equilibrium, as some investigators have accepted [2, 3].

If such is the case, then in the equilibrium state, the combined rate of formation of sulfonic acid and sulfonyl chloride will be equal to zero, i.e.,

$$\frac{dx_5}{dt} = 0 \text{ and } \frac{dx_6}{dt} = 0, \text{ hence:}$$

$$K_3AY_E[B - A(2-Y)] = K_4A(1-Y_E)[C + A(1-Y_E)]$$

or

$$\frac{Y_E}{1-Y_E} = \frac{K_4}{K_3} \cdot \frac{C + A(1-YE)}{[B - A(2-Y_E)]} = K_E \cdot \frac{C_E}{B_E} . \tag{9}$$

Thus, the ratio of sulfonic acid and sulfonyl chloride yields in the state of presumed equilibrium should be determined by the ratio of the reaction rate constants (4) and (3), and by the ratio of sulfuric acid concentration in the equilibrium state, C_E, to the concentration of chlorosulfonic acid, B_E.

Let us examine upon what the ratio of sulfuric acid to chlorosulfonic acid in that state depends:

$$\frac{C + A(1-Y_E)}{B - A(2-Y_E)} = \frac{\frac{C}{A} + (1-Y_E)}{\frac{B}{A} - (2-Y_E)}$$

Hence it can be seen that the yields of sulfonic acids and of sulfonyl chlorides in the state of presumed equilibrium, along with other factors, are determined (primarily) by the ratio of initial concentration of sulfuric acid to that of sulfonating agent $\frac{C}{A}$, and by the ratio of initial concentration of chlorosulfonic acid to sulfonating agent $\frac{B}{A}$.

Let us find the derivative for the function $\frac{dx_4}{dt}$, equating it to zero, and using the specifically determined value, Y, from the resulting equation which corresponds to the extreme value for the function, and let us substitute it into the function. We thereby get interesting results which have significant practical value, namely:

$$\left(\frac{dX_4}{dt}\right)_{extr} = -K_4 \cdot \frac{C^2}{4}.$$

Hence it can be seen that the extreme value for the decomposition rate of sulfuric acid and sulfonyl chloride (a process undesirable from the standpoint of practical production of chlorosulfonate) is a value which depends upon the initial concentration of sulfuric acid at the second stage.

These conclusions refute the claim of L. S. Solodar and Z. I. Shevchenko [1] that sulfuric acid does not play any role in the chlorosulfonation and that this is in complete agreement with their experimental data, with those of Spryskov [2, 3], and with those of the present author.

In using Equation (9), the author assumed that the system is in equilibrium. We might examine the accuracy of this assumption.

Take sulfonic acid, chlorosulfonic acid and sulfuric acid in the initial stage, where their concentrations are respectively equal to S, B. and C. Assume during the time, t, that X moles of sulfonic acid are converted to the sulfonyl chloride. In this case there is formed X moles of sulfonyl chloride and X moles of sulfuric acid, which interact further according to Reactions (3) and (4).

It should be taken into account in this case that the reaction between sulfonyl chloride and sulfuric acid actually proceeds in part with evolution of sulfur trioxide and hydrogen chloride, and not with evolution of chlorosulfonic acid, as was assumed by Spryskov [2, 3].

In fact, if one proceeds from sulfonyl chloride and pure sulfuric acid, rather than from a mixture of sulfuric acid and chlorosulfonic acid, then the reaction will proceed until such time when all of the sulfonyl chloride has converted to the sulfonic acid, and no equilibrium between sulfonyl chloride and sulfonic acid can be observed.

Equations of rate for Reactions (3) and (4) in the units adopted can be presented as follows:

$$\frac{dx_3}{dt} = K_1 (S-X)\cdot(B-X),$$

$$\frac{dx_4}{dt} = K_2 \cdot X(C+X), \text{ where } K_2 = K_2(\leftarrow) + K_2(\rightarrow).$$

The equation for the overall process rate will be:

$$\frac{dx}{dt} = K_1(S-X)\cdot(B-X) - K_2X(C+X). \qquad (10)$$

To simplify the conclusions, let us take C = 0 and S = B = 1, whereupon Equation (10) will be expressed:

$$\frac{dX}{dt} = K_1(1-X)^2 - K_2X^2. \qquad (11)$$

As X increases, the first member of the equation decreases, and consequently the second will increase, and at a determined value for X, the rate sum of the process can become equal to zero, which will define a "pseudoequilibrium" state for the system. In fact, modified curves of the $\frac{dx}{dt}$ function in relation to X, as represented in Fig. 1, pass through zero with a free selection of K_1 and K_2 values (taken within the range observed for the experiment). However, this state is not found to be truly an equilibrium, but rather a "pseudoequilibrium", inasmuch as further course of Reactions (3) and (4) takes the system out of this state, and the modified rate for sulfonyl chloride quantity (X) with time acquires a negative value, which indicates decrease in the amount of sulfonyl chloride after passage through a maximum.

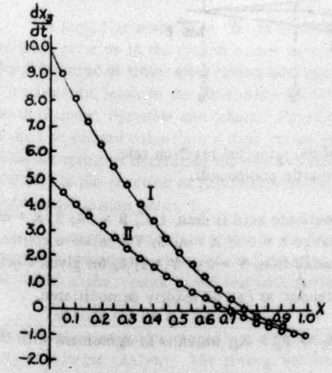

Fig. 1. Calculated curves for Function (11) Modification. I.) For $K_1 = 10$ and $K_2 = 1$; II) for $K_1 = 5$ and $K_2 = 1$.

Inasmuch as in Reaction (3) the concentration of chlorosulfonic acid decreases continuously, while the concentration of sulfuric acid increases, nonetheless, a decrease in sulfuric acid concentration during the course of Reaction (4) does not lead to a corresponding increase in concentration of chlorosulfonic acid, and the hydrogen chloride which is evolved leaves the zone of interaction, in which case the actual equilibrium state will, of course, be the state of the process, i.e., at that state where there will be present in the reaction mixture the following concentrations: chlorosulfonic acid, 0; sulfonyl chloride, 0; sulfonic acid, S, sulfuric acid, C + B.

Consequently, in the general case where C ≠ 0 and S ≠ B ≠ 1 a pseudoequilibrium state is possible:

$$\frac{dx}{dt} = 0 \quad K_1(S-X_{PE})(B-X_{PE}) = K_2X_{PE}(C+X_{PE}),^*$$

hence

$$\frac{X_{PE}}{S-X_{PE}} = \frac{K_1}{K_2}\cdot\frac{B-X_{PE}}{C+X_{PE}} = K_{PE}\cdot\frac{B-X_{PE}}{C+X_{PE}} \qquad (12)$$

i.e., the ratio of sulfonyl chloride to the amount of sulfonic acid in the pseudoequilibrium state depends upon the ratio of reaction rate

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[*] Subscript PE = pseudoequilibrium.

constants and the ratio of chlorosulfonic acid concentration to the sulfuric acid concentration at the end of the process, and depends only upon those factors we have already mentioned.

To reach high yields of sulfonyl chloride in chlorosulfonation practice, a high concentration of chlorosulfonic acid should be maintained and a low concentration of sulfuric acid, the process should be interrupted at the pseudoequilibrium state, and should be carried out at such temperature conditions as $K_1 \gg K_2$.

Solution of Equation (12) in relation to X_{PE} gives:

$$X_{PE} = \frac{K_{PE}(B + S) + C \pm \sqrt{[K_{PE}(B + S) + C]^2 - 4(K_{PE} - 1)K_{PE}BS}}{2(K_{PE} - 1)},$$

which is in agreement with the formula developed by Spryskov [2] with regard to the true equilibrium state. It actually however, should be regarded as a reflection of the sulfonyl chloride concentration in the "pseudoequilibrium" state.

To determine the form of the summated rate process curve, we can graphically present the individual reaction rates (1, 2, 3, and 4) according to the rate equations (5, 6, 7 and 8) for the process at random values A, B, C, K_1, K_2, K_3 and K_4 selected within the range found in chlorosulfonation practice (Fig. 2).

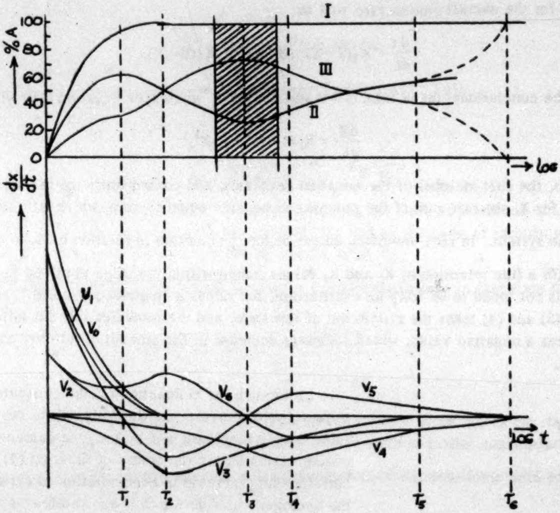

Fig. 2. Graphical presentation of a mathematical analysis of the principal reaction rate (1)-(4) equations which occur during chlorosulfonation of aromatic compounds.

We shall take into account here that: 1) a large excess of chlorosulfonic acid is used, i.e., $B > 2A$; 2) X = degree of sulfonation of the substance, which can be changed within the range $X = 0$ to $X = A$; 3) Y = relative content of sulfonic acid in the mixture of sulfonated compounds, and can be varied from $Y = 0$ to $Y = 1$; 4) for given changes in the variable X and Y, the $\frac{dx_1}{dt}$, $\frac{dx_2}{dt}$, $\frac{dx_3}{dt}$ and $\frac{dx_4}{dt}$ functions are continuous, as can be readily demonstrated.

Let us assume that: $K_1 > K_2$, $K_3 > K_4$ and $K_2 \gg K_3$, i.e., $K_1 > K_2 \gg K_3 > K_4$, which is in agreement with the experimental data.

The curves are plotted for the system $\frac{dx}{dt} - \log \underline{t}$.

Functions (5), (6), (7) and (8) are represented by the curves $\underline{v}_1$, $\underline{v}_2$, $\underline{v}_3$ and $\underline{v}_4$, respectively, (lower curves in Fig. 2); $\underline{v}_1$ and $\underline{v}_2$ are plotted up from the abscissa axis, reflecting processes of accumulation in the reaction mixture of sulfonic acid and sulfonyl chloride; curves $\underline{v}_3$ and $\underline{v}_4$ are tentatively plotted downward from the abscissa axis, inasmuch as they reflect the reactions involving loss of these same substances.

Let us reproduce a graphical construction of the modified curves for the rate of conversion of the sulfonated compound $\underline{v}_0 = \underline{v}_1 + \underline{v}_2$, which changes the rate of sulfonic acid formation with simultaneous run of all processes: $\underline{v}_5 = \underline{v}_1 - \underline{v}_3 + \underline{v}_4$ and of sulfonyl chloride $\underline{v}_6 = \underline{v}_2 + \underline{v}_3 - \underline{v}_4$.

By carrying out a graphical integration of the functions obtained, we can construct curves I, II, and III (upper curves of Fig. 2) which express the change with time: I = amount of compound sulfonated (by $\underline{v}_0$), II = amounts of sulfonic acids formed (by $\underline{v}_5$), III = amount of sulfonyl chloride formed (by $\underline{v}_6$).

Let us analyze the resulting curves.

Curve I increases rapidly up to point T_2, whereupon it reaches a maximum value equal to A (100%), and then proceeds parallel to the abscissa axis, inasmuch as $\underline{v}_0 = 0$.

Curve II has a maximum at point T_1, since $(\underline{v}_5)_{T_1} = 0$, and it then begins to decrease because the rate of sulfonic acid formation becomes negative. At point T_3, the curve is at a minimum $(\underline{v}_5)_{T_3} = 0$, and then increases to maximum value at point T_6.

Curve III increases all the time up to point T_3, where it possesses a maximum, inasmuch as $(\underline{v}_6)_{T_3} = 0$. Beyond that, the rate of formation of sulfonyl chloride ($\underline{v}_6$) becomes negative, in connection with which the curve gradually falls, reaching 0 at point T_6.

Thus, the graph for the summated process has along the time axis the four following characteristic points.

Point T_1, in which the formation rate for sulfonic acid is equal to zero at the same time that the formation rate for sulfonyl chloride is not equal to zero. The points correspond to the maximum quantity of sulfonic acid formed. In the experiments, this point was not attained when time, T_2, was too short, especially at elevated temperature.

Point T_3 is the second characteristic point at which $(\underline{v}_5)_{T_3} = 0$ and $(\underline{v}_6)_{T_3} = 0$. This point corresponds to the maximum amount of sulfonyl chloride formed for a minimum quantity of sulfonic acid. Point T_3 is the pseudo-equilibrium point, and is not a true equilibrium, inasmuch as beyond this point $\underline{v}_4 - \underline{v}_3 \neq 0$.

Point T_5 is the third characteristic point, because it corresponds to the zero rate for the following processes: $(\underline{v}_3)_{T_5} = 0$ while rates for the other processes are other than 0.

Point T_6 is the point of final state for the process because at this point the rates for all of the processes are equal to zero.

This point corresponds to that state where there is no chlorosulfonic acid in the system, and all of the sulfonyl chloride has been converted to the sulfonic acid. The system consists of only three components – sulfuric acid, sulfonic acid and sulfur trioxide.

It should be mentioned that in the period of time close to T_3 (shaded in the figure), the change in amount of sulfonyl chloride in the system occurs very slowly. Determination of the amount of sulfonyl chloride in the system for this period of time, after taking into account experimental and analytical errors, gives almost constant results. This situation leads to the conclusion that a number of investigators have taken this period to be the true equilibrium state (Solodar, Spryskov and others). Partially erroneous conclusions were drawn to the effect that chlorosulfonation should be carried out within a time period not less than that determined, and that longer time for the reaction course does not result in decreasing the yield of sulfonyl chloride [6]. As can be seen, such a viewpoint of the problem is harmful to the practice of chlorosulfonation. The process should be interrupted at a point as close as possible to the pseudoequilibrium point, T_3.

To verify conclusions drawn on the basis of an analysis of the kinetic equations, the author undertook to experimentally investigate change in the quantity of sulfonyl chloride over an interval of time, reacting the chlorosulfonic acid with diphenylurea at 25° and with acetanilide at 25° and 40°.

The diphenylurea was purified by two recrystallizations from absolute ether, and the acetanilide from alcohol. Technical chlorosulfonic acid was distilled in vacuo (78-80° at 21-25 mm) and contained 98.1% of $ClSO_3H$ according to chlorine analysis. The process was carried out in a thermostat and to maintain a specified temperature, solid carbon dioxide was introduced into the reaction mixture at the start of the reaction to remove heat of reaction. After determined intervals of time, the sulfonic mixture was aspirated into an ampoule, the latter sealed and broken under water in a closed vessel. Calculation of the sulfonyl chloride formed was carried out on the basis of determination of "inorganic" and "organic" chlorine, utilizing the Volhard method. The resulting data are given in Fig. 3.

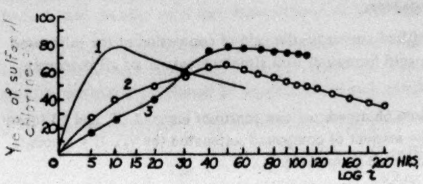

Fig. 3. Dynamics of change in quantity of sulfonyl chlorides in the reaction mixture during chlorosulfonation. 1) Acettanilide at 40°; 2) acetanilide at 25°; 3) diphenylurea at 25°.

A comparison of the curves constructed according to experimental data with the integral curves analytically constructed (Fig. 2) indicates sufficiently good coincidence in the nature of the curves.

Characteristic for these curves, aside from the extreme points, is the presence of deflection points, both for ascending and descending branches of the curves.

The presence of these points confirms the complex mechanism for the process and the coexistence of a number of reactions whose courses are varied. This confirms the accuracy of the reaction mechanism, determined by the author, which occurs upon chlorosulfonation of aromatic acyl amines [5], which is expressed by aggregate of Equations (1)-(4).

SUMMARY

1. A mathematical analysis of the rate equations for individual reactions which occur upon chlorosulfonation of aromatic acylamines has been carried out according to the mechanism determined earlier by the author [5]. The resulting integral curves of molar amounts of sulfonyl chloride changing with time in the reaction mixture agree well with the curves constructed from experimental data for chlorosulfonation of acetanilide and of diphenylurea.

2. It has been determined that the aromatic compound-chlorosulfonic acid system comes to a pseudoequilibrium state with time, which can be maintained unchanged for a prolonged length of time relative to the amounts of sulfonyl chloride and sulfonic acid, and this was earlier considered erroneously to have been the true equilibrium state.

3. It has been demonstrated that the maximum yield of sulfonyl chloride is reached at the pseudoequilibrium state, and is determined by the ratio between the reaction rates (3) and (4). Consequently, for a given compound and temperature, it is determined by the relation of chlorosulfonic acid and sulfuric acid concentrations to the concentration of chlorosulfonated compound.

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* See Consultants Bureau Translation, page 787.

** See Consultants Bureau Translation, page 2097.

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POLAROGRAPHIC INVESTIGATION OF THE HYDROGENATION PROCESS

II. HYDROGENATION OF MALEIC AND FUMARIC ACID MIXTURES

A. L. Markman

The behavior of cis- and trans-ethylenes is an individual problem in catalytic hydrogenation of ethylene compounds. Paal and Schiedewitz [1], Ott [2], and Golendeev and Plisov [3], who hydrogenated, individually, various geometric isomers, have found that the saturation rate for cis-isomers is always higher than for trans-isomers.

The author has not found in the literature information on the behavior of cis- and trans-isomers when they are hydrogenated as combined mixtures; nor any general description on combined hydrogenation experiments. The author, therefore, undertook a study of the behavior of maleic and fumaric acids during their separate and their combined hydrogenation.

Maleic acid was prepared from chemically-pure maleic anhydride and purified by three recrystallizations from aqueous solution. After drying, the m.p. was 130°. The fumaric acid was chemically-pure when used.

The author carried out a number of experiments on separate hydrogenations of the acids named with platinum and with palladium catalysts which were precipitated onto aluminum and nickel supports, as the result of which the hydrogenation rate constants were determined, which are given in Table 1. The experimental procedure was the same as described earlier [4].

It can be seen from Table 1 data that the relationship of the saturation rate constants for maleic and fumaric acids to the nature of the catalyst, and its amount, varies over quite a wide range —from 0.92 to 9.29, and in the majority of cases, maleic acid saturates more rapidly than fumaric acid.

In the hydrogenation of maleic-fumaric acid mixtures, the author has developed a method for their combined polarography. The author has established that these acids give two different waves upon reduction at the dropping mercury cathode, in absolute ethyl alcohol acidified with 0.1 N hydrochloric acid, and which differ in the half-wave potential values by 0.2 V, the difference amounting to 0.17-0.18 V in 95-96% alcohol. This circumstance was utilized by the author to analyze mixtures of maleic and fumaric acids during the course of their hydrogenation.

TABLE 1

Expt. No.	Acid hydrogenated (0.005 mole)	Catalyst	Amount of catalyst (in mg)	Metal support	Amount of metal support (in mg)	Hydrogenation rate constants	Ratio of the constants, $k_{maleic}/k_{fumaric}$
157 153	Maleic Fumaric	Pd	32	Ni	105	0.088 0.960	0.92
45 152	Maleic Fumaric	Pd	64	Ni	105	0.188 0.082	2.29
103 154	Maleic Fumaric	Pd	32	Al	105	0.0468 0.0071	6.59
107 155	Maleic Fumaric	Pd	64	Al	210	0.0613 0.0066	9.29
19 16	Maleic Fumaric	Pt	58	Ni	105	0.0190 0.0095	2.00

The sequence of carrying out experiments on combined hydrogenation of the two geometrically isomeric acids is given.

1. Hydrogenation of Maleic-Fumaric Acid Mixture with Palladium Catalyst

Experiment 104. 0.58 g of maleic and 0.58 g of fumaric acids (in 1/200 mole portions), 210 mg of Al and 64 mg of Pd, 30 ml of alcohol in 10 ml water. Bath temperature was 25°, air temperature 14°, pressure 717.5 mm, theoretical volume of hydrogen absorbed, H_0, was 252.8 ml. For the polarography, 1 ml of each sample was dissolved in 25 ml of the medium (0.1 N HCl in 96% alcohol). $\pi_{1/2}$ for maleic acid) 0.72 V, and for fumaric acid, 0.89 V. The concentration of each acid in the polarographed solution for sample No. 1, as sampled before hydrogenation, was equal to $0.005 = 500 \cdot 10^{-5}$ moles/liter. For convenience and for unity of concentration of the polarographed solutions, the concentration $1 \cdot 10^{-5}$ moles/liter was adopted. Then for the case investigated, the concentration of each acid, C, in relative units, was equal to 500.

During the course of hydrogenation, 12 samples were taken and polarographed. By measurement of the polarographic wave heights for both acids, their concentrations in each sample were determined, after which the reaction mixture composition following each consecutive state of hydrogenation, was calculated. The resulting data are given in Table 2.

TABLE 2

Sample No.	H_2 absorbed (in %)	Maleic acid		Fumaric acid		Composition of mixture (in %)		
		C	saturation (in %)	C	saturation (in %)	maleic acid	fumaric acid	succinic acid
1	0	500	0	500	0	50.0	50.0	0
2	8.3	420	16.0	500	0	42.0	50.0	8.0
3	17.0	338	32.4	500	0	33.8	50.0	16.2
4	25.7	250	50.0	500	0	25.0	50.0	25.0
5	34.7	198	60.4	456	8.8	19.8	45.6	34.6
6	43.8	134	73.2	428	14.4	13.4	42.8	43.8
7	53.3	58	88.4	410	18.0	5.8	41.0	53.2
8	63.1	47	90.6	323	35.4	4.7	32.3	63.0
9	73.3	0	100	267	46.6	0	26.7	73.3
10	83.6	0	100	164	67.2	0	16.4	83.6
11	98.2	0	100	58	88.4	0	5.8	94.2
12	100.0	0	100	0	100	0	0	100

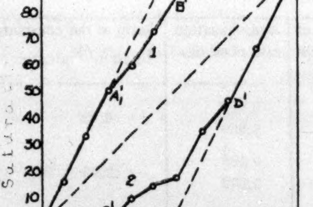

Fig. 1. Characteristics of selectivity of the hydrogenation process for a mixture of unsaturated compounds, using Pd and 25°. 1) Maleic acid; 2) fumaric acid. Explanations in the text.

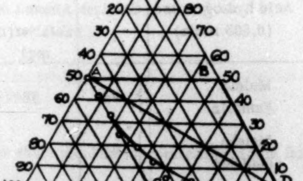

Fig. 2. Change in composition of the reaction mixture upon hydrogenation of the acids. M.A. = Maleic Acid; F.A. = Fumaric Acid; S.A. = Succinic Acid.

On the basis of the data in this Table, the curve (Fig. 1) was constructed. If the saturation process were completely unselective, then the saturation curve for each component of the mixture should coincide with the diagonal, AD. With completely selective saturation, for example of maleic acid, its saturation should proceed along the broken line, ABD, and fumaric along the line ACD. Actually, the saturation curves showed certain deviations from the absolute selectivity.

Of special interest in connection with this fact is the nature of the degree of selectivity of the process.

A method for relating the content of saturated fatty acids in a fat with the iodine number [5] is well known, or a similar method for combining the iodine and thiocyanogen numbers for a fat, which have been applied to fats.

The A. A. Zinovyev method is of considerable interest, according to which the degree of selectivity is characterized by the ratio of the constants for the rate of saturation of both components of the mixture: $K=\frac{K_1}{K_2}$ [6]. However, it would have been more convenient, in the author's opinion to select the value, $1-K$, to characterize the process. This value for a completely selective process is equal to 1, if completely unselective, 0, and for any other it acquires a value lying between 0 and 1, and therefore, is closer to 1 the more selective the process.

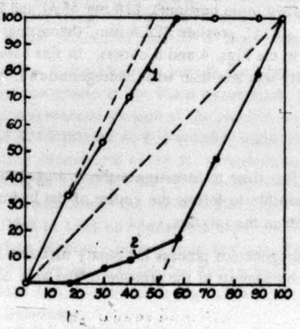

Fig. 3. Characterization of the degree of selectivity of the hydrogenation process for unsaturated acids, using Pd and at 40°. 1) Maleic acid; 2) fumaric acid. Explanation in the text.

Inasmuch as each pair of curves for unsaturated compounds is constructed analogously to the one presented in Fig. 1, for purposes of clarity, it is possible, therefore, to characterize the degree of selectivity by the area defined by the closed curve, AA'B'DD'C', and the area of the parallelogram, ABDC. Apparently, in a strictly selective process, when saturation of one of the components of the mixture takes place along the broken line, ABD, and the second component along the broken line, ACD, this ratio becomes equal to 1; in a completely unselective process, where both compounds become saturated along the straight line AD, the ratio and the degree of selectivity are equal to 0; in the remainder of cases the degree of selectivity lies between 0 and 1. In the particular case of fumaric and maleic acids, according to experimental data from the 104th experiment, the degree of selectivity was found to be equal to $S=\frac{41.05}{50}=0.821$, where 41.05 and 50 are the areas for the figure (in cm^2).

Measurement of the areas of the figures with their irregular shape, is accomplished by means of a planimeter. Without a planimeter, this problem can be solved by gravimetric procedure.

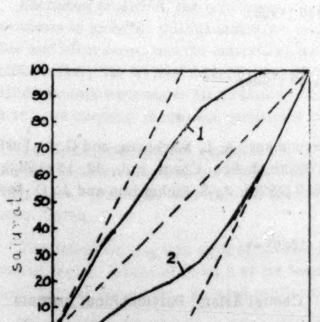

Fig. 4. Characterization of the degree of selectivity of the hydrogenation process for a mixture of unsaturated compounds, using Pt at 24°. 1) Maleic acid; 2) fumaric acid. Explanations in text.

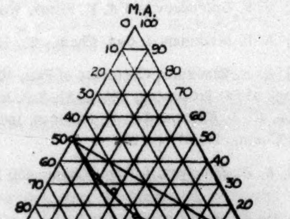

Fig. 5. Change in composition of the reaction mixture upon hydrogenation of the acids. F.A. = fumaric acid; M.A. = maleic acid; S.A. = succinic acid.

The change in composition of the reaction mixture, in agreement with the values in the last three columns of Table 2, is presented in a triangular coordinate system in Fig. 2. Point A corresponds to initial composition of the mixture; point D = the product from complete saturation. The transition from point A to point D can be realized by various routes: along the broken line, ABD, under the conditions of selective steric saturation, first with fumaric and then with maleic acid; along the broken line ACD with a strictly selective hydrogenation, first of maleic and then of fumaric; and along the straight line, AD, under conditions of completely unselective hydrogenation.

In the author's experiment, the points corresponding to composition of mixtures in a number of consecutive hydrogenation stages are distributed most closely to the broken line, ACD, on the AD curve. This indicates that the process proceeds with almost complete selectivity, maleic acid being saturated first, and then fumaric.

Similar experiments at 40° indicated a higher degree of selectivity, S = 0.874 (Fig. 3).

2. Hydrogenation of a Mixture of Maleic and Fumaric Acids with Platinum Catalyst

Experiment 158. A mixture of maleic and fumaric acids (in 1/200 mole portions), 210 mg of Al and 232 mg of Pt, 30 ml of alcohol in 10 ml of water. Bath temperature was 24°, air 11°, pressure 726.5 mm, theoretical hydrogen absorption, H_0, 243.8 ml. Results of the hydrogenation are given in the Figs. 4 and 5 curves. In this case, again maleic acid saturates predominately; however, the degree of selectivity was less than with hydrogenation in the presence of palladium catalyst (S = 0.686).

SUMMARY

1. The method of polarographic analysis has been used for the first time to investigate the hydrogenation process for mixtures of unsaturated organic compounds, which makes it possible to follow the course of the hydrogenation, and in particular the distribution of hydrogen between components in the mixture.

2. A method for quantitatively expressing selectivity of the hydrogenation process for binary mixtures by determining the ratio of figure area circumscribed by saturation curves for components of the mixture to the area corresponding to absolute selectivity of the process (S index) has been used.

3. It has been determined that for mixtures of geometrically-isomeric acids (maleic and fumaric) the first hydrogenates selectively for the most part, and selectivity is more pronounced when working with palladium catalyst than with platinum; however, in none of these cases does it bear an absolute character.

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* See Consultants Bureau Translation, page 1699.

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YULY SIGIZMUNDOVICH ZALKIND

Kh. V. Balyan

The 23rd of November, 1953, marks five years from the day of the tragic death of one of the most talented representatives of the older generation of Russian organic chemists, Yuly Sigizmundovich Zalkind, professor, doctor of chemical sciences, honored scientist and technician of the RSFSR, who was head of the organic chemistry department of the Leningrad Institute of Technology, awarded the Red Banner of Labor.

Yu. S. Zalkind was born in the city of Vilno on December 14, 1875, the son of a pharmacist. In 1894, having finished the course at the Vilno gymnasium, Zalkind entered St. Petersburg University, where he graduated in 1898, in the natural science section of the physico-mathematical faculty, with a diploma of the first rank. On the recommendation of Academician A. E. Favorsky, whose student Zalkind became, in 1899 he was appointed assistant in the organic chemistry department of the St. Petersburg Institute of Technology, which, from 1898 on, was headed by A. E. Favorsky. Beginning in 1934, when A. E. Favorsky was forced to leave the department as the result of overwork, Zalkind was its head. In addition to the technological institute, Zalkind carried on educational work in other academic institutions. From 1908 to 1918 he headed the department of organic chemistry and was dean of the chemical faculty of the St. Petersburg Women's polytechnic institute. From 1918 to 1920 he was professor at the Perm State University. He also worked in Leningrad at the 2nd Polytechnic and 1st Medical Institutes, and headed the department of organic chemistry of the A. I. Gertsen pedagogical institute. During World War II (1942-1944), Zalkind was professor at the Tiflis State University.

In 1914 Yu. S. Zalkind defended a master's thesis on the subject "The Action of Magnesium on Esters of Halogen-Substituted Carboxylic Acids," while in 1935, the Presidium of the Academy of Sciences of the USSR conferred on him the degree of doctor of chemical sciences for his scientific work as a whole. The scientific-educational work of the deceased lasted almost fifty years.

Enormous erudition, the continuous supplementing of his lectures with information concerning the very latest achievements of science, skillful exposition of the lectures in a brilliant yet, at the same time, universally comprehensible and clear form, were the outstanding traits of Zalkind as teacher in institutions of higher education and as a scientific worker. He trained a large group of scientific workers. The number of Zalkind's students who studied scientific research work under his direction, exceeds 80 persons. In the period since 1935 alone, forty bachelors theses and two doctoral theses were completed under the direction of Zalkind and presented.

Yu. S. Zalkind was the author of one of the best textbooks of organic chemistry, which has run through four editions and has been prepared for a fifth. The textbook was posthumously translated into the Azerbaidzhan and Georgian languages. Under his editorship 19 assorted manuals, monographs and textbooks were translated and issued in the Soviet Union.

The scientific research work of Zalkind took place not only within academic walls, but also in research institutes and factory laboratories such as the State Institute of Applied Chemistry, the Plastics Institute, the "Red Triangle" factory and others. Zalkind published more than 200 works and received 20 author's certificates.

The themes of his first two works, on aldehydes and ketones [1, 3] were suggested to Zalkind by his teacher A. E. Favorsky. Jointly with Professor Wallach he completed one work on a subject chosen by Zalkind himself: "The Production of Methylcyclohexanone" [2]. From then on, Zalkind, already embarked on a career of independent research, created his own school of organic chemists.

The numerous works of Zalkind, grouped by subject, are briefly considered below.

ORGANO-MAGNESIUM COMPOUNDS

Many years of research, finally published in the form of a monograph, were dedicated to the study of the action of magnesium on esters of halogen-substituted acids [204]. Zalkind, in contradistinction to other chemists, based his study entirely on the action of magnesium on compounds of complex structure, in which two or more atoms of halogen were found, or, along with them, nitrogen or oxygen atoms. It was of interest, on the one hand, to elucidate to what extent such compounds were suitable for organomagnesium syntheses, and on the other hand, to find the mobility of the halogen and its reactivity in relation to the structure of the organic molecule. He studied the behavior of esters of various halogen acids – saturated, mono- and di-basic, aromatic (with the carboxyl in the nucleus and in the side chain), with the halogen in the α- and in the β-positions. The action of magnesium on these compounds was found to be not always consistent. In some cases substituted acetoacetic ester was produced, for example tetramethylacetoacetic ester, while in others the ester of atropic acid, the ester of phenylacetic acid, and also benzyl alcohol and diphenylacetic ester were formed, i.e., in some cases the halogen of the original ester was replaced by hydrogen.

Proceeding from theoretical considerations concerning the influence of carboxyl groups on halogen mobility in the molecule of such acids, Zalkind hypothesized that moving away the halogen from the carboxyl ought to lead to greater mobility of the halogen and, consequently, ought to be accompanied by increased reactivity of the organomagnesium compound. These hypotheses were confirmed by study of the action of magnesium on esters of the β-bromo and β-iodo-acids [6, 14], when it was established that these halogen esters give as chief reaction products the esters of the corresponding dibasic hydroxy acids. For example, in the reaction of magnesium with the ether ester of β-bromo-β-phenylpropionic acid, by the way first synthesized by Zalkind, the products were: diphenyladipic ester (9.4%), hydrocinnamic ester (26.5%) and the ethyl ester of a dibasic hydroxyacid (47.4%) with the following structure:

$$C_6H_5-CH_2-CH_2-C(OH)[CH(C_6H_5)-CH_2-COOC_2H_5]_2.$$

The esters of aromatic halogen acids with the halogen and the carboxyl group in the nucleus, entirely fail to react with magnesium [16], with the exception of the ethyl ester of o-bromobenzoic acid, which reacted with magnesium, although with difficulty, and, like the β-halogen esters, gives as chief product the corresponding lactone acid. The esters of halogen acids with the halogen in the nucleus and the carboxyl in the side chain also show very weak activity of the halogen, while, on the contrary, the esters with the carboxyl in the nucleus and the halogen in the side chain react more actively with magnesium and act like the analogous β-halogen esters.

Zalkind also investigated the action of magnesium on esters of halogen-substituted dibasic acids, for example the methyl and ethyl esters of bromosuccinic acid [17]. The main reaction rapidly proceeds according to the pattern of the β-halogen esters, in other words, the inhibiting influence of the carboxyl group on the reactivity of the MgBr group observed with α-halogen esters, is not observed here. In the above investigations two further important observations were also made concerning: 1) the oxidizability of products of organomagnesium compounds, and 2) the saponification of complex esters by the action of activated magnesium or of the etherate of magnesium iodide [7].

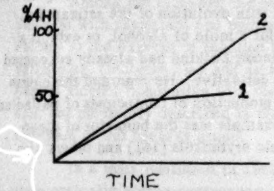
Zalkind also conducted other investigations with magnesium. Thus, he developed a new method for preparing ketones (by the actio of magnesium on the salt of the acid [9]), and studied the action of magnesium on dihalogen aromatic compounds [40, 56, 74, 80].

It was shown, in contrast to the data of other authors, that bromine can also react with magnesium, though the reaction rate depends on the structure. Zalkind for the first time, proposed a simple method for preparing monomagnesium bromoacetylene and its use for the usual synthesis [33]. Thus, methylphenylacetylenylcarbinol $CH_3C(C_6H_5)(OH)C{\equiv}CH$ [33, 126], was synthesized for the first time by its reaction with acetophenone. His work concerning the dependence of the rate of reaction between dimagnesiumdibromoacetylene and carbonyl compounds in the preparation of acetylenic γ-glycol [118]; on the replacement of alkoxy groups by alkyl groups by the action of magnesium iodoethylate on dimethyl and diethyl ethers of diacetyl γ-glycol [157]; on the production of α-bromotoluic acid, synthesized for the first time by him [15], and other work, is also of interest.

ADDITION OF HYDROGEN TO ACETYLENE DERIVATIVES

This group of researches was considerably greater in extent and in importance. For this work Yu. S. Zalkind, in due time, was honored with the F. E. Dzerzhinsky prize. The first work of Zalkind on the hydrogenation of the acetylenic γ-glycol – 2,5-dimethyl-hexyne-3-diol-2,5, commonly called tetramethylbutynediol, had already led to the very interesting phenomenon of an action of colloidal palladium that was selective in comparison with that of platinum black [10]. With the former catalyst the addition of only two atoms of hydrogen per mole of glycol with evolution of ethylene glycol proceeds rapidly, after which the speed of hydrogenation rapidly diminishes – a sudden change in rate sets in. In the presence of platinum, however, the addition of hydrogen proceeds smoothly with absorption of 2 moles of hydrogen by 1 mole of glycol and evolution of the saturated glycol. This is particularly evident from the figure, where, on the ordinate axis is plotted the quantity of added hydrogen in per cent, reckoning 2 moles of hydrogen per 1 mole of glycol, and on the abscissa – the duration of hydrogen absorption in minutes.

Zalkind and his co-workers dedicated more than 50 works to the further investigation of this interesting question. Various acetylenic glycols, alcohols, their compound and simple esters [17, 19-26, 28, 29, 31, 32, 42, 45, 49, 50, 54, 65-68, 69, 73, 84, 91, 98, 99, 110, 114, 126, 130, 138, 139, 144, 147]; acetylenic erythritols, hydroxy-acids, hydrocarbons [30, 34, 41, 83, 125, 129]; diacetylenic glycols, alcohols, erythritols, compounds with some multiple bonds and others [27, 89, 93-95, 115-117, 120, 128, 133, 136, 141, 143, 153, 156], were synthesized for these investigations. Very many representatives of these groups of compounds, and often the first representative of a whole new class, were synthesized for the first time by Zalkind. As a result of the hydrogenation of acetylenic glycols, ten new ethylenic and saturated glycols were produced, and the method of hydrogenating acetylenic glycols in the presence of colloidal palladium was replaced by a new and very convenient method for the synthesis of varied ethylenic glycols and their derivatives, including their geometric isomers. Prior to the work of Yu. S. Zalkind, ethylenic glycols were not generally known.



Catalytic hydrogenation of tetramethyl butynediol.
1) Hydrogenation in the presence of palladium. 2) hydrogenation in the presence of platinum.

It was established that the above-mentioned selective character of the action of the catalyst is present in the hydrogenation of all acetylenic γ-glycols and depends only on the chemical nature of the metal and not on its physical state; it does not depend on the nature of the carrier – a protective colloid [65], nor on the temperature of hydrogenation, the quantity of catalyst, nor on the quantity or nature of the solvent [19]. All these conditions only influence the rate of hydrogenation, as well as the structure of the glycol itself, that is, the speed of hydrogenation depends, in particular, on the weight and character of the glycol radicals. Glycols with various radicals and diverse arrangements and combinations, symmetrical and asymmetrical, ditertiary, disecondary, secondary-tertiary and so forth, were investigated.

It is interesting to note that the majority of these glycols were prepared by Zalkind by the method of Zh. I. Iotsich,(with whom he was associated in a collaboration of many years standing in the laboratory of A. E. Favorsky), from bromodimagnesiumbromoacetylene and the appropriate aldehyde or ketone.

It was established that disecondary and secondary-tertiary γ-glycols are hydrogenated considerably faster than ditertiary γ-glycols. The rate of hydrogenation falls in a given series with increased weight of the radical [20, 91], asymmetric radicals are hydrogenated faster than symmetric [21, 67]; stereochemical factors also influence the rate of hydrogen addition [11, 83, 84]. The behavior of *a*-glycols in hydrogenation differs markedly from the behavior of γ-glycols. Thus, in the hydrogenation of the *a*-glycol – 1,2,4-triphenylbutyne-3-diol-1,2, $C_6H_5-CHOH-C(OH)(C_6H_5)C\equiv C-C_6H_5$ in the presence of colloidal palladium, although the speed of hydrogenation is reduced in the second half of the reaction, the sharp discontinuity characteristic of γ-glycols is not observed. In this respect *a*-glycols are almost like acetylenic [22] and diacetylenic [27] alcohols, which, with platinum black or colloidal palladium, are smoothly hydrogenated, uniformly adding 4 or 8 atoms of hydrogen per mole of alcohol, and forming alcohols of the saturated series.

In this fashion the characteristic course of hydrogenation of acetylenic γ-glycols is specifically dependent on symmetrically distributed hydroxyls on the carbon atoms located on both sides of the triple bond. This conclusion does not apply to glycols of the diacetylenic series, as is evident from work begun during the life of Zalkind and published after his death. Thus, in hydrogenation with colloidal palladium, the glycol – 2,7-dimethyloctadiyne – 3,5-diol-2,7, as well as its methyl and ethyl ethers [153, 156] does not give the characteristic discontinuity in hydrogenation rate after the addition of 4 atoms of hydrogen.

The esterification of acetylenic γ-glycols precisely repeats the course of their hydrogenation in the presence of colloidal palladium. The acetic esters of disecondary glycols are thus hydrogenated faster than the glycol itself, but esters of ditertiary glycols, on the contrary, add hydrogen with more difficulty than the glycols [114, 139]. The simple esters do not act in a similar manner in hydrogenation: one of them is hydrogenated with more difficulty, the other more readily, than the glycols [144, 147, 154].

Only two of the acetylenic hydrocarbons undergo hydrogenation: phenylacetylene and diphenylacetylene [30, 34]. They differ markedly in the course of their reaction both from the behavior of γ-glycols and from each other. With phenylacetylene the triple bond is hydrogenated rather slowly, while the double bond generates styrene. On the other hand, in the hydrogenation of diphenylacetylene, the reaction goes smoothly and some retardation is observed, only just before the end of the reaction. In both cases hydrogenation of the benzene nucleus also takes place.

Hydrogenation of several alcohols with vinyl acetylene radicals of the type $R_2C(OH)-C\equiv C-CH=CH_2$ showed that in the presence of platinum black they smoothly add 6 atoms of hydrogen with evolution of the saturated alcohol, but with colloidal palladium they either add only 4 atoms of hydrogen for 1 mole of alcohol, or exhibit a strongly retarded reaction after addition of 4 atoms of hydrogen. This phenomenon Zalkind had already accounted for, not by the character of the catalyst, but by the properties of the ethylenic derivative. He regarded the course of hydrogenation as consisting of five independent stages, of which the rate of production of compounds of palladium with acetylenic and ethylenic derivatives was limiting [120, 133]. Such, for example was the behavior of diene hydrocarbons [95]. Some acetylenic hydroxyacids and their amides [125], acetylenic erythritols [141] and others also conducted themselves in a fashion different from that of the γ-glycols.

The study of the action of some organic additives in the hydrogenation of acetylenic alcohols and glycols is related to this series of researches and gave rise to a series of interesting observations, noted for the first time in the literature [138].

In a series of general articles and reports, Zalkind dwelt in detail on the explanation and interpretation of the mechanism of hydrogenation, on the problem of the mathematical expression of the hydrogenation rate, and so forth [171, 174, 177, 196].

INVESTIGATIONS OF THE PROPERTIES OF ACETYLENIC AND ETHYLENIC GLYCOLS

The first work of Zalkind in this field dealt with the study of the action of concentrated sulfuric acid on acetylenic γ-glycols and the corresponding ethylenic and saturated glycols, and also on the oxides and their acetic esters [18]. Observing, under these conditions, a considerably increased intensity of color, , Zalkind elucidated the influence of multiple bonds, but failed to find oxygen in the γ-position, as had been maintained before him. This conclusion was based on the study of the action of sulfuric acid on several acetylenic, diacetylenic and saturated alcohols. The action of a dilute alcohol solution of sulfuric acid on asymmetric dimethyldiphenylbutynediol proved interesting; in addition two isomeric products were prepared – a ketone of the tetrahydrofuran series and an α-diketone with an open chain of carbon atoms [151].

In a series of researches Zalkind elucidated the action of hydrohalogen acids on acetylenic γ-glycols [35-39, 48, 52] and established that the action, for example, of hydrogen bromide, may proceed in two directions: on the one hand, dibromide with two double bonds may be evolved (occasionally some isomeric dibromides) and on the other hand – the evolution of substituted monobromodihydrofuran is possible. The action of the halogens – bromine, chlorine – on various glycols, which leads to a complex mixture of products, was also studied [142, 154].

Examination of the action of halogens, of bromine in particular, on various glycols of the ethylenic series gave very interesting results [44, 51, 61, 64, 109]. In these reactions, products of diverse structure were produced in all cases, often depending on the stereochemical relationships; the corresponding dibromides, dihydroxybromides, or saturated monohydroxybromides were chiefly produced. The addition of chlorine and bromine to 2,3-diphenyl-butadiene-1,3 [119], may be associated with this same series. Not without interest is the work of Zalkind on the addition of carboxylic acids to acetylenic γ-glycols [123], which he undertook in connection with the capacity of acetylene to add carboxylic acids at the site of the triple bond with formation of vinyl esters. Indeed, the tetramethylbutyndiol investigated by him added to acetic acid in the presence of mercury salts, but in addition formed two products: tetramethyltetrahydroketofurane and the acetic ester of tetramethyldihydroxyfuran.

In his last years Zalkind became interested in the work of his pupil V. K. Teterin, who had demonstrated that water is eliminated by heating benzyl alcohol in the presence of activated clay and dibenzyl ether, and that further transformation products are formed. If sulfanilic acid is taken as the catalyst, the sole product of the reaction is dibenzyl ether. World War II and the resulting death of V. K. Teterin, deprived Teterin of the possibility of continuing these investigations. However, these results stimulated Zalkind to study the condensation of acetylenic glycols and alcohols with phenols.

The first subject of investigation was the study of the action of phenol on tetraphenylbutynediol in the presence of these same catalysts [135]. As a result a mixture of products was obtained consisting of four crystalline substances and a resin. The resin was not further investigated, but the crystalline substances were demonstrated to be derivatives of dihydrofuran, indene and indenochromane. The condensation of tetramethylbutynediol with phenol [148] led to the formation of two products, apparently dihyrofuran derivatives. The condensation of symmetric and asymmetric dimethyldiphenylbutynediol with phenol in the presence of sulfanilic acid [152, 155] proceeds in various directions: in the first case a mixture of six products is produced, a portion of which represented derivatives of dihydrofuran, and in the second case, phenol is added readily at the site of the triple bond of the glycol and formation of a dihydrofuran ring proceeds with proportional elimination of water.

Among the alcohols, the condensation of benzyl alcohol with phenol and several of its derivatives [150], and also with resorcinol and pyrocatechol [146] was investigated. In the first case the condensation proceeded chiefly at the expense of reaction between phenol and alcohol. In the second case in place of the previous, activated clay, Georgian clay and ascanite (clay activated with sulfuric acid) were applied. It was established that benzyl alcohol condensing with resorcinol and pyrocatechol in the presence of ascanite forms dihydroxydiphenylmethane, not previously described in the literature, and that the benzyl radical enters the benzene nucleus in the position para to the hydroxy group.

In a work published in 1949 [145], he demonstrated the conditions for the separation of racemic glycols from optically active components by means of fractional crystallization from optically active bornylacetate ester.

INVESTIGATIONS OF DERIVATIVES OF POLYNUCLEAR COMPOUNDS (NAPHTHALENE, PHENANTHRENE)

Zalkind, with his coworkers, devoted more than 15 investigations to bromoderivatives of naphthalene and several of its substituted derivatives. He spoke for the first time on this question at the Mendeleev Congress in 1928. The problem of the structure of the dibromonaphthalenes prepared by the action of bromine on naphthalene interested him. A whole array of foreign authors had studied this question before him. However, in spite of the large number of researches, it was impossible to determine precisely how many isomeric dibromides of naphthalene there were, and exactly what was produced in the direct bromination of naphthalene. The basic failure of the previous investigations was the absence of data on the influence of reaction conditions on the isomer yield. This gap was filled by the work of Zalkind which was developed with quite definite regularity. The yield of 1,4-dibromonaphthalene (m.p. 82°) was the greater the milder the reaction conditions [53]. On the other hand, many disputes had been provoked by a bromination product of naphthalene with a m.p. 67-68°. Zalkind demonstrated that this product represented a eutectic mixture of the 1,4- and 1,5-dibromonaphthalenes and indicated the conditions for obtaining the 1,4- and 1,5-dibromonaphthalenes with relatively greater yields [82]. In this same work he defined more accurately the problem of the products generated by heating dibromonaphthalene with $AlCl_3$ in a stream of HCl, and showed the errors of one of the investigators of this point. In another of his works, Zalkind established that 1,4,6-tribromonaphthalene is obtained by the bromination of 1,4-dibromonaphthalene [57]. The very interesting observation was made at the same time that nitration and sulfonation of the 1,4-dibromonaphthalene lead to a nitroproduct with a nitro group in position 5, while the sulfo group was again located in position 6. This, at first glance unusual, phenomenon, stimulated Zalkind to occupy himself with the study of the mutual influence of substituents in the naphthalene nucleus. As a result of this it was established that the order of substitution into the naphthalene nucleus is determined by: 1) the directive action of the substituents already present, 2) the activity of the α-atom and 3) the comparative stability of the two rings which constitute the naphthalenic ring structure. These conclusions were subsequently verified and confirmed by him in a series of specially conducted experimental investigations [70, 75, 76].

Out of a desire to close the gap in the investigation of the problem of the relation between molecular structure and capacity for polymerization, Zalkind studied the polymerization of α- and β-vinylnaphthalene and several homologs of the former [90, 106]. It was established that the homologs of α-vinylnaphthalene are considerably less polymerized than α-vinylnaphthalene itself, and in addition that the polymerization proceeds in another direction: α-vinylnaphthalene gives a polymer, but its homologs give only a dimer.

Zalkind's inclination to study unexplored fields and to expand the sources of expensive raw materials for the organic chemical industry led him to investigate a series of phenanthrene derivatives. In 1927 he succeeded in synthesizing for the first time 9-iodophenanthrene [46], and later studied the preparation conditions and the properties of nitrophenanthrenes [62], and phenanthrylamines [87]. Zalkind conducted very interesting studies on the catalytic oxidation not only of phenanthrene [100], but also of several other aromatic compounds [97]. Azo dyes of the phenanthrene series [134] and several alcohols of this same series not described in the literature [149] were prepared and studied.

SYNTHESES OF GEOMETRIC ISOMERS OF ETHYLENIC GLYCOLS, ASYMMETRIC GLYCOLS AND ERYTHRITOLS OF THE ACETYLENIC AND DIACETYLENIC SERIES

Zalkind published the first report of the formation of two geometric isomers of tetramethylbutenediol $(CH_3)_2C(OH)CH{=}CHC(OH)(CH_3)_2$ in 1916 and 1923, although in 1913 he had already noted that, in the hydrogenation of tetramethylbutyne diol in the presence of colloidal palladium, after the addition of 2 atoms of hydrogen per molecule of glycol, crystals of tetramethylbutenediol with a m.p. of 76.5 - 77° were formed, while crystals with a much lower melting point separated from the mother liquor. These isomers he designated the α-form (maleinoid) and the β-form (fumaroid) [24]. It was shown that the relative quantity of these isomers depends on the hydrogenation rate, and that their formation represents a primary phenomenon, that is, that each form arises independently in the process of hydrogenation. It was the first case of stereochemical isomerism without internal rearrangement in the direct addition of hydrogen to acetylenic glycols under mild conditions (in the absence of acids and alkalis). These studies aroused objections on the part of several foreign chemists. In subsequent detailed work [42, 49, 66, 68, 96, 99] on the basis of new experimental data and explicit theoretical considerations, Zalkind refuted these objections and corroborated his observations and conclusions.

In 1927 Zalkind published a modest but interesting article on the synthesis of the first representative of the class of erythritols of the acetylenic series until then not described in the literature. The erythritol was prepared by the action of dimagnesiumdibromoacetylene on benzoin with a yield of 63% of the theoretical [41]. In 1948, a new report appeared on another synthesis – concerning the preparation of the first representative of the diacetylenic series of erythritols, which was formed by the reaction of the magnesium derivative of the acetylenic alcohol with benzil [141].

A very interesting synthesis was that of an asymmetric glycol of the type unknown in the literature, $R_2C(OH)-C{\equiv}C-C(OH)R'_2$ by a common method: the action of a dimagnesium derivative of acetylene on a mixture of two distinct ketones or on a mixture of an aldehyde with a ketone. In such a fashion various asymmetric glycols were synthesized and investigated [45, 66, 67, 69, 73, 126, 151, 152].

THE INVESTIGATION OF HIGHLY UNSATURATED COMPOUNDS WITH MANY MULTIPLE BONDS (TRIPLE OR DOUBLE)

From 1930 Zalkind directed his attention to the investigation of compounds of the general formula C_nH_{2n-4} and compounds even poorer in hydrogen having a considerable capacity for polymerization; several of them, according to their structure close to vitamin A, had been only slightly investigated, but interest in them rose in relation to the necessity of utilizing condensation products of acetylene. After he had clarified the conditions for preparation of the magnesium derivatives of vinylacetylene $CH_2{=}CH-C{\equiv}C-MgBr$ [79], Zalkind utilized it for the synthesis of the corresponding alcohols from acetone, ethyl acetate and β-ionone [81]. He prepared the magnesium derivative of acetylenyldivinyl and synthesized from it and acetone the corresponding tertiary alcohol [128]. These alcohols underwent dehydration (with production of slightly polymerized hydrocarbons) and hydrogenation. This was shown to be a convenient method for preparing alcohols with three double bonds in a side radical.

Diphenyldiacetylene was prepared by the action of an acidified solution of cuprous chloride on phenylacetylene in the presence of NH_4Cl, and this subsequently appeared to be a very convenient general method for preparing diacetylenic hydrocarbons [89, 93, 116]. Substituted phenylacetylenes with substituents of type I, which induce a certain electron density in the ortho and para positions, readily enter into similar condensations, but with substituents of type II, they condense with more difficulty than phenylacetylene itself [116].

It was later shown that similar behavior was characteristic of monosubstituted acetylenes and of acetylenic alcohols, which made it possible to propose a new method for preparing glycols of the diacetylenic series [117]. Thus, for example, the diacetylenic glycol – 2,7-dimethyl-octadiyne-3,5-diol-2,7 – was produced from dimethylacetylenylcarbinol by the action of cuprous chloride in the presence of NH_4Cl. It is interesting to note that the secondary acetylenic alcohols undergo less condensation under the indicated conditions: Zalkind explained this phenomenon from the electronic point of view.

Diacetylenic glycols on heating with solid alkali, $Ba(OH)_2$, MgO, decompose similarly to the acetylenic glycols with evolution of the diacetylenic alcohols which appears to be a convenient method for producing them.

For example, from $(CH_3)_2C(OH)-C\equiv C-C\equiv C-C(OH)(CH_3)_2$ was produced 5-methyl-hexadiyne-1,3-ol-5 $(CH_3)_2C(OH)-C\equiv C-C\equiv CH$ [115].

Two more investigations of Zalkind in the field of highly unsaturated compounds should be mentioned: the investigation of the dehydration of methyldiphenylacetylenylcarbinol, which led to the polymerized product of the hydrocarbon $(C_6H_5-C\equiv C)_2C=CH_2$ [124], and the study of the rearrangement of 1-phenylpentadiene-2,4-ol-1 $C_6H_5-CHOH-CH=CH-CH=CH_2$, which, as was shown, in the very moment of formation by the hydrogenation of vinylacetylenic alcohol, isomerizes, possibly in two directions, in particular with the formation of the unsaturated primary alcohol. This demonstrated that allyl rearrangement can spread along a conjugated chain [136].

INVESTIGATIONS INTIMATELY RELATED TO TECHNOLOGICAL PROBLEMS

A larger number of Zalkind's works can be referred to the category of those intimately related to the direct demands and needs of technology and industry. To this question Zalkind and his coworkers devoted more than 35 works, and received, in addition, 20 author's certificates.

Here one may find works in the fields of aniline dyes, the technology of resins, the chemistry and technology of solvents, essential oils, petroleum, and in particular the field comparatively young in our country, of the plastics industry [63, 71, 72, 77, 78, 85, 87, 92, 101-103, 105, 107, 108, 111-113, 121, 122, 127, 131, 132, 134, 171, 173, 175, 176, 180]. A number of his contributions are used by industry at the present time (the preparation of camphor from turpentine, styrene, tetrachlorophthalic acid and others). It is necessary to note that the works of this series were begun only in the postrevolutionary period and were all the more widely disseminated as our country's socialist economy grew.

From the pen of Zalkind came a series of articles, notes, reports concerning new developments in chemistry and chemical technology, concerning the lives and scientific activity of the leaders of Russian chemical thought – A. E. Favorsky [181, 185-187], A. E. Porai-Koshits [188], B. V. Byzov [182], the life and work of Zh. I. Iotsich [195], about whom there was little information in the literature, and others.

In addition to his scientific-educational activity, Yu. S. Zalkind carried on active work in various public fields.

At the end of the last century Zalkind became one of the first teachers of physics and chemistry at the Sunday evening classes for workers in the village of Smolensk (near the Neva gate to St. Petersburg) and continued this activity gratis for a duration of 12 years. For a number of years Zalkind worked in the trade union elective agency of the Leningrad Lensoviet Institute of Technology; he was chosen deputy from the collective of the latter to the thirteenth convocation of the Leningrad Soviet. From 1899, Zalkind was a member of the Russian Physico-Chemical Society (now the All-Union D. I. Mendeleev Chemical Society); from 1932 he was a member of the Council of societies, and from 1938 to the day of his death he was an alternate representative of the Leningrad section. In addition, for a period of 13 years Zalkind was a member of the editorial board of the Journal of General Chemistry.

The students and scientific collective of the Lensoviet Institute of Technology welcomed with great affection and warmth Zalkind's speeches, interesting as to content and stylistically brilliant, at general meetings of the institute on diverse general, political and scientific questions. His highly fruitful and useful work was frequently recognized by the leaders of the Institute, the ministries and the Leningrad Soviet. In 1937 Zalkind was awarded a valuable grant and diploma by the central committee of the LYCLSU.

The government decorated Yu. S. Zalkind with the order of the Red Banner of Labor, the medal "For valiant work in the Great Patriotic War, 1941-1945" and in 1947 conferred on him the title of Honored Scientist and Technician of the RSFSR.

Those who knew Yu. S. Zalkind, and very many chemists, engineers, physicians and teachers knew him, will always remember the talented investigator, the brilliant lecturer, the outstanding leader and teacher, the charming conversationalist, the sensitive, sympathetic comrade, the indefatigable toiler in the Soviet higher schools, the founder of a school of organic chemists.

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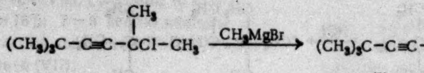
THE SYNTHESIS OF BRANCHED-CHAIN ALKINES

THE PREPARATION OF 2,2,3,3,6,6-HEXAMETHYLHEPTYNE-4

A. I. Zakharova and G. M. Murashov

The synthesis of acetylenic hydrocarbons with two or more quaternary carbon atoms has as yet been little studied. Meanwhile, the question of the extent to which the structure of such hydrocarbon compounds affects the triple bond reactivity is of interest. From another point of view, these hydrocarbons may serve as starting material for the synthesis of difficultly available paraffins containing quaternary carbon atoms in their molecules.

The first representative of alkines with 2 quaternary carbon atoms – ditertiary butylacetylene (2,2,5,5-tetramethylhexyne-3) (I) was prepared in 1946 by Hennion and Banigan [1] by the action of methylmagnesium bromide on 2,2,5-trimethyl-5-chlorohexyne-3.

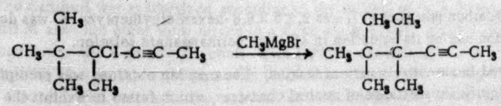


$$(CH_3)_3C-C\equiv C-\overset{CH_3}{\overset{|}{C}}Cl-CH_3 \xrightarrow{CH_3MgBr} (CH_3)_3C-C\equiv C-C(CH_3)_3$$

(I)

As the hydrocarbon was hard to hydrogenate, it was initially converted into the corresponding olefin by means of hydrogenation under pressure in the presence of Raney nickel catalyst, and then coverted into the paraffinic hydrocarbon by pressure hydrogenation in the presence of palladium on carbon. By oxidizing the hydrocarbon with an aqueous solution of potassium permanganate, ditertiary butyl ketone was produced instead of trimethylacetic acid. In general the triple bond in this hydrocarbon was not successfully hydrated.

The second representative of alkines with two quaternary carbon atoms – 2,2,3,3-tetramethylhexyne-4 (II) was prepared by Zakharova and Sapozhnikova [2] by the action of methylmagnesium bromide and 2,2,3-trimethyl-3-chlorohexyne-4.



$$CH_3-\overset{CH_3}{\underset{CH_3}{C}}-\underset{CH_3}{C}Cl-C\equiv C-CH_3 \xrightarrow{CH_3MgBr} CH_3-\overset{CH_3}{\underset{CH_3}{C}}-\overset{CH_3}{\underset{CH_3}{C}}-C\equiv C-CH_3$$

(II)

The hydrocarbon was not oxidized by an aqueous solution of potassium permanganate at ordinary temperatures.

The entire literature on the question of the synthesis and characteristic properties of alkines with two quaternary atoms in the molecule is apparently confined to these two examples. Tertiary acetylenic chlorides of the type $(R)_2CCl-C\equiv C-R$, due to their great reactivity, proved to be very suitable starting materials for the synthesis of such hydrocarbons, while attempts to prepare the ditertiary butylacetylene (I) by the action of a Grignard reagent on the dichloride corresponding to the tetramethylbutynediol $(CH_3)_2CCl-C\equiv C-CCl(CH_3)_2$, did not lead to positive results [1, 3].

Recently published work by A. D. Petrov and O. N. Lavrischeva [12], which demonstrated that acetylenic dichlorides, prepared from high molecular γ-acetylenic glycols (for example, the dichloride corresponding to dimethylditertiarybutylbutynediol), enter into the Grignard reaction, is of great interest in this connection. The authors prepared a series of highly branched alkines with four quaternary carbon atoms.

At the same time it is necessary to keep in mind (as the work of one of us demonstrated [2, 4])that reaction with organomagnesium compounds of tertiary acetylenic chlorides with a methyl group in an α-position to the triple bond, of the type $(R)_2CCl-C\equiv C-CH_3$ (III), is accompanied by molecular rearrangement, and consequently, tetrasubstituted allenes are formed along with the methyl hydrocarbon.

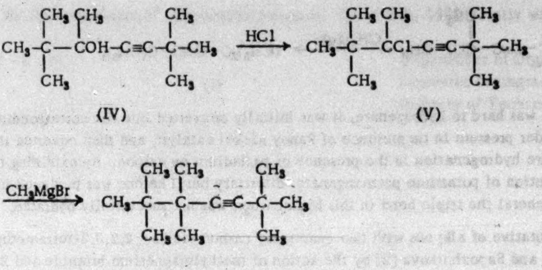
In connection with these considerations, the goal of the present work was clarification of the course of the reaction between methylmagnesium bromide and the tertiary acetylenic chloride – 2,2,3,6,6-pentamethyl-3-chloroheptyne - 4 -(V), having in an α - position to the triple bond a tertiary butyl group, and to determine whether the reaction would proceed normally, or would be accompanied by molecular rearrangement.

Interest in this reaction was further due to the possibility that it might be relied on for production of the first representative of acetylenic hydrocarbons containing three quaternary carbon atoms in the molecule.

An acetylenic tertiary alcohol – 2,2,3,6,6-pentamethylheptyne-4-ol-3 (IV) prepared by us for the first time served as starting material for the present investigation. The alcohol was produced according to the A. E. Favorsky reaction by the action of tertiarybutylacetylene on pinacolin in the presence of powdered alkali (KOH) in ether. The carbinol was transformed by the action of gaseous hydrogen chloride into the tertiary chloride (V). It turned out that the carbinol (IV) with a tertiary butyl-group in an α - position to the triple bond also reacts mildly with gaseous hydrogen chloride, as we have repeatedly noted for tertiary acetylenic carbinols containing the grouping $>COH–C≡C–CH_3$ [2, 5]. The yield of the chloride (V) reached 86% of theoretical.

The sole product obtained as a result of the reaction between the chloride (V) and methyl magnesium bromide corresponded in molecular weight and elementary analysis fo the formula $C_{13}H_{24}$.

By the study of the Raman spectrum, it was established that the hydrocarbon obtained belonged to the alkine series. Its spectrum has the intense frequency (2223 cm^{-1}) characteristic of the triple bond.

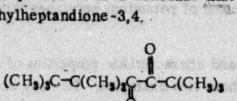


(IV) (V)

(VI)

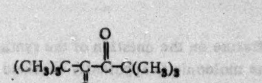
That the structure of the hydrocarbon produced (VI) was 2,2,3,3,6,6-hexamethylheptyne-4, was demonstrated by its ozonization in chloroform solution and by its oxidation in alkaline permanganate solution.

The ozonization did not proceed in an entirely normal fashion. The ozonide obtained was precipitated by decomposition as a quantitatively insignificant substance of neutral character, which failed to exhibit the usual carbonyl-group reactions. By ultraviolet spectroscopic investigation, it was established that this substance possessed a maximum absorption in the neighborhood of λ = 2880, 2980 and 3630 Å (ϵ = 45.7, 44.2 and 17.0, respectively) (see figure). These data permitted us to conclude that the substance was an α-diketone, apparently of structure (VII) – 2,2,5,5,6,6-hexamethylheptandione-3,4.



$$(CH_3)_3C-C(CH_3)_2C(=O)-C(=O)-C(CH_3)_3$$

(VII)



$$(CH_3)_3C-C(=O)-C(=O)-C(CH_3)_3$$

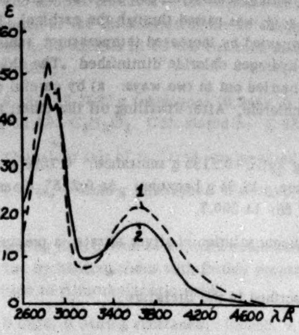
(VIII)

According to data of Leonard and Mader [6], the absorption spectrum in the near ultraviolet region for the structure – 2,2,5,5-tetramethylhexandione-3,4 (VIII) is characterized by the presence of an absorption band with a maximum near λ = 2850, 2940 and 3650 Å(ϵ = 52.5, 47.0 and 21.0 respectively).

In addition, in an aqueous solution of the ozonolysis products, the presence of formaldehyde was established by the dimedone test.

Two acids were separated from the acidic products of ozonization: dimethyltertiarybutyl acetic acid, identified by its melting point, analysis of the acid itself, and of its silver salt, and trimethylacetic acid, identified by analysisis of its silver salt.

In the preparation of the silver salts, formation of a silver mirror was observed, which showed the presence



Ultraviolet absorption curves of: 1 – 2,2,5,5-tetramethylhexandione-3,4 (VIII) (according to data of Leonard and Mader [6]); 2 – A neutral substance, obtained by ozonization and oxidation of 2,2,3,3,6,6-hexamethylheptyne-4 (VII).

of formic acid in the decomposition products of the ozonide. The presence of formic acid was also verified by Fincke's method [7].

The presence of formaldehyde and formic acid in the ozonolysis products is apparently explained by an anomalous course of ozonization.

The hydrocarbon is oxidized by alkaline solution of permanganate only by prolonged heating on a boiling water bath. The presence in the products of oxidation of trimethylacetic acid in the form of its silver salt and of an α-diketone (VII) identical with the α-diketone obtained by ozonization, was established; this was apparent on comparison of their ultraviolet absorption spectra.

As is evident from the course of the reactions of ozonization and oxidation, the triple bond in the hydrocarbons produced was very inert, which is evidently due to the over-all structure of the molecule.

Spectroscopic investigation of the hydrocarbon (VI), and also determination of its physico-chemical constants demonstrated that it was an individual component. No data indicating that it contained even the faintest admixture of quaternary allenic hydrocarbon were obtained.

On this basis one may conclude that reaction of the chloride (V) with methylmagnesium bromide proceeds normally and is not accompanied by molecular rearrangement.

EXPERIMENTAL

The Preparation of 2,2,3,6,6-Pentamethylheptyne-4-ol-3 (IV)

The carbinol was synthesized according to the method of A. E. Favorsky. 150 g of powdered caustic potash and 200 ml of absolute ether were mixed in a three-necked flask, quickly furnished with a rotary propeller mixer, a reflux condenser and a dropping funnel. With rapid agitation and external cooling to 0°, a solution of tertiary butylacetylene* (0.5 mole) and pinacolin (0.5 mole) in 50 ml of absolute ether were introduced in drops in the course of 5 hours. The reaction mass was left for 15 hours and then decomposed in water with cooling and agitation. The ethereal layer was separated from the alkaline solution and dried with anhydrous sodium sulfate. The ether was distilled off, and the remaining product subjected to vacuum distillation. Two fractions were obtained, the first with a boiling point 30-60° at 8 mm pressure, and the second with a boiling point of 74-77° at 8 mm. About 2 g of unreacted pinacolin was separated from the first fraction by redistillation After two redistillations, the acetylenic carbinol (IV) was obtained from the second fraction with a yield of 60% of theoretical. The carbinol crystallized on standing.

M.p. 22°; b.p. 75° at 8 mm, 82° at 15 mm; d_4^{25} 0.8321; n_D^{25} 1.43742; n_α^{25} 1.43495; n_β^{25} 1.44358; n_γ^{25} 1.44819. MR_D 57.45; MR_α 57.16 MR_β 58.15; MR_γ 58.67. $C_{12}H_{22}O^{\overline{F}}$. Calculated : MR_D 57.07; MR_α 56.83; MR_β 57.78; MR_γ 58.31. σ^{25} 25.10; P 490.4. Calculated 500.4 (C); 501.8 (M and F).

0.0530 g substance: 0.1532 g CO_2; 0.0615 g H_2O. 0.0506 g substance: 0.1463 g CO_2; 0.0570 g H_2O. 0.1366 g substance: 21.47 g benzene: Δt 0.18°. 0.1976 g substance: 21.47 g benzene: Δt 0.26°. Found %: C 78.83, 78.85; H 12.98, 12.60; M 181.3, 181.5. $C_{12}H_{22}O$. Calculated %: C 79.05; H 12.16; M 182.2.

2,2,3,6,6 Pentamethylheptyne-4-ol-3 had not been described in the literature.

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*For preparation of tertiary-butylacetylene, see [8, 9].

Preparation of 2,2,3,6,6-Pentamethyl-3-chloroheptyne-4 (V)

25 g of carbinol (IV) (in portions of 5 g each) was treated with gaseous hydrogen chloride while cooled. The hydrogen chloride, prepared by heating concentrated hydrochloric acid, was passed through the carbinol. Initially the reaction progressed with complete absorption of the gas, accompanied by increased temperature; subsequently the reaction mixture crystallized by degrees and the absorption of hydrogen chloride diminished The chloride formed was pressed out on a porous plate. Its purification may be carried out in two ways: a) by careful sublimation, b) by solution in ether and drying the ether solution with calcium chloride. After distilling off the ether, the chloride was vacuum distilled. The yield was 86% of the theoretical.

M.p. 52°; b.p. 82° at 15 mm; 0.3324 g substance: 0.2338 g AgCl. 0.2195 g substance: 0.1596 g AgCl. 0.0999 g substance: 16.94 g benzene: Δt 0.15°. 0.1418 g substance: 16.94 g benzene: Δt 0.215°. Found %: Cl 17.40, 17.98; M 201.5, 199.6. $C_{12}H_{21}Cl$. Calculated%: Cl 17.66; M 200.7.

The chloride is readily hydrolyzed. On shaking with an aqueous solution of silver nitrate, a precipitate of AgCl is formed.

2,2,3,6,6-Pentamethyl-3-chloroheptyne-4 had not been described in the literature.

The Preparation of 2,2,3,3,6,6-Hexamethylheptyne-4 (VI)

The Grignard reagent was prepared as usual from 8 g of Mg and 50 g of methylbromide in 150 ml of ether. With continuous agitation, 50 g of the chloride (V) dissolved in 100 ml of absolute ether was added; simultaneously there was a moderate heating of the reaction mixture, and the flask was externally cooled with ice water.

The mixture was left for 14 hours, after which it was warmed on a water bath at 40° for 2 hours, and then decomposed with water with hydrochloric acid added. The ethereal solution of the hydrocarbon was separated, dried with anhydrous sodium sulfate, and the ether distilled off. The hydrocarbon remaining after vacuum distilling four times over metallic sodium (until the Beilstein reaction for halogen was negative) was a colorless, mobile liquid (yield 55% of theoretical) and had the following constants:

B.p. 48° at 6 mm; d_4^0 0.8016; d_4^{20} 0.7643; n_D^{20} 1.43326; n_α^{20} 1.43066; n_β^{20} 1.43977; n_γ^{20} 1.44523. Found: MR_D 61.35; MR_α 61.03; MR_β 62.15; MR_γ 62.82. $C_{13}H_{24}|\!\equiv$. Calculated: MR_D 60.17; MR_α 59.90; MR_β 60.86; MR_γ 61.52; EM_D 1.18*; $\omega_{\alpha\beta}$ 21.0.

0.0750, 0.0708 g substance: 0.2377, 0.2253 g CO_2; 0.0931, 0.0877 g H_2O. 0.1650, 0.3218 g substance: 16.92 g benzene: Δt 0.28, 0.54°. Found %: C 86.44, 86.78; H 13.88, 18.85; M 178.6, 180.6. $C_{13}H_{24}$. Calculated %: C 86.58; H 13.42; M 180.3.

2,2,3,3,6,6-Hexamethylheptyne-4 had not been described in the literature.

The Raman Spectrum of the Hydrocarbon (VI)**. 150 (4), 170 (4), 242 (1), 565 (3), 608 (7), 795 (3), 815 (0.5), 847 (2), 905 (3), 926 (8), 1201 (5), 1228 (5), 1394 (0.5), 1447 (10), 2223 (10), 2273 (1), 2919 (4), 2972 (5).

The Ozonization of the Hydrocarbon (VI). 5 g of the hydrocarbon was ozonized in a solution in 80 ml of purified chloroform to the cessation of ozone absorption. The solvent was distilled off in a vacuum (10-15 mm) while heated on a water bath at 20-25°. The ozonide was cautiously decomposed with boiling water containing a sevenfold quantity of sodium carbonate. By steam distillation of the neutral products of ozonolysis, a small quantity of a greenish oil was prepared which failed to give a precipitate when treated with a solution of acetic semicarbazide. An α-diketone structure (VII) for this substance was confirmed by the ultraviolet absorption spectrum*** (see the figure).

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* The presence of a greatly heightened molecular refraction in highly branched alkines has already been noted in the literature [10].

** The Raman spectrum was taken with a Zeiss triprism glass spectrograph: the excitation line was the 22,938 cm^{-1} Hg line (with a ZhS-2 glass filter), the slit aperture was 0.07 mm, the exposure was 4 hours. The intensity was visually evaluated on a 10-point scale.

*** The ultraviolet spectrum was taken with a non-registering photoelectric spectrophotometer SF-11 (Beckmann type) in 95% ethanol: The concentration was 0.01 mole / liter, the thickness of the cell was 1 cm.

In addition, the presence of formaldehyde (to 10%) was established by the dimedone reaction.

The neutral products of the solution which remained after distillation were oxidized with sulfuric acid. At the beginning of the distillation of the acidic products, crystals of dimethyltertiarybutylacetic acid, insoluble in water, and quite soluble in all the common solvents, were collected. After drying and distillation, the acid melted at 182°.*

0.1005, 0.0592 g substance: 0.2450, 0.1438 g CO_2; 0.0997, 0.0613 g H_2O. Found %: C 66.48, 66.25; H 11.10, 11.58. $C_8H_{16}O_2$. Calculated %: C 66.56; H 11.18.

The silver salt of the acid was prepared via the ammonium salt and its analysis gave the following results:

0.0251, 0.0520 g substance: 0.0108, 0.0223 g Ag. Found %: Ag 43.03, 42.88. $C_8H_{15}O_2Ag$. Calculated %: Ag 42.97.

During distillation of volatile acids from the acid products, several fractions of about 5 ml each were collected, and by heating them with freshly prepared silver carbonate, silver salts were prepared, corresponding in composition to trimethylacetic acid.

0.0325, 0.0459 g substance: 0.0168, 0.0236 g Ag. Found %: Ag 51.69, 51.42. $C_5H_9O_2Ag$. Calculated %: Ag 51.62.

In addition, on heating the acidic solution with silver carbonate, a silver mirror was formed, which indicated the presence of formic acid. The presence of formic acid (to 20%) was also ascertained by Fincke's method [7].

SUMMARY

1. The tertiary acetylenic alcohol – 2,2,3,6,6-pentamethylheptyne-4-ol-3 (IV) – was produced and characterized for the first time by condensation of tertiary butylacetylene with pinacolin according to the method of A. E. Favorsky.

2. The corresponding chloride – 2,2,3,6,6-pentamethyl-3-chloroheptyne-4 (V) was produced and characterized for the first time by the action of dry hydrogen chloride on the carbinol (IV).

3. Reaction of the chloride (V) with methyl magnesium bromide produced the first representative of the group of highly branched alkines with three quaternary carbon atoms in the molecule – 2,2,3,3,6,6-hexamethylheptyne-4 (VI). The structure of this hydrocarbon was demonstrated by its ozonization and oxidation and also by investigation of its Raman spectrum.

4. It was established that, in the given case, molecular rearrangement did not occur at the moment of reaction in organomagnesium synthesis.

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* According to data in the literature [11], dimethyl-tertiary butylacetic acid has a sublimation temperature of 80° and a m.p. of around 200°.

** See Consultants Bureau Translation, page 1843.

*** MSU = Moscow State University.

**** See Consultants Bureau Translation, page 75.

***** See Consultants Bureau Translation, page 1633.

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* See Consultants Bureau Translation, page 1175.

ACETYLENE DERIVATIVES. 163

THE HYDRATION OF VINYLACETYLENE IN ALCOHOLIC SOLUTIONS

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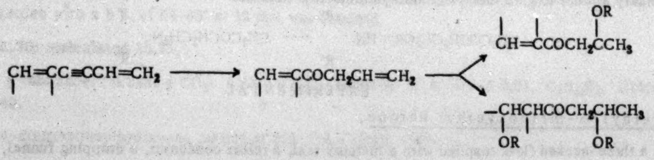
It was earlier established by us that divinylacetylenic hydrocarbons are readily hydrated in alcoholic solutions (in the presence of mercury sulfate and sulfuric acid) into the corresponding vinylallyl ketones, which add one or two molecules of alcohol and are converted into β-alkyoxy ketones [1].



It was of interest to examine the possibility of hydration under analogous conditions of vinylacetylene with the object of preparing the corresponding methyl-β-alkoxyethyl ketones.

The hydration of vinylacetylene into methylvinyl ketone was accomplished for the first time by Nieuwland [2], and was investigated in more detailed by Churbakov and Ryazantsev [3].

$$CH{\equiv}CCH{=}CH_2 \xrightarrow[HgSO_4]{H_2O} CH_3COCH{=}CH_2.$$

N. Kozlov and K. Krechko [4] prepared methylvinyl ketone with a yield of 75-85% of the theoretical by shaking a 10% solution of vinylacetylene in toluene with 25% sulfuric acid in the presence of 1-2% mercury sulfate.

Nieuwland [5] prepared methyl-β-methoxyethyl ketone by addition of methanol to methylvinyl ketone in the presence of trichloroacetic acid functioning as a catalyst.

$$CH_3COCH{=}CH_2 + CH_3OH \xrightarrow[CCl_3COOH]{} CH_3COCH_2CH_2OCH_3.$$

As a result of the present investigation, we have established that in alcohol solutions vinylacetylene is very readily hydrated to methylvinyl ketone which, under the experimental conditions, adds one molecule of alcohol with formation of the corresponding methyl-β-alkoxyethyl ketones.

$$CH{\equiv}CCH{=}CH_2 \xrightarrow[HgSO_4]{H_2O\ +ROH} CH_3COCH{=}CH_2 \longrightarrow CH_3COCH_2CH_2OR.$$

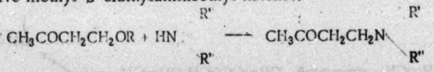
The hydration reaction was brought about by passing vinylacetylene into a boiling alcohol-water solution containing mercury sulfate and sulfuric acid as catalyst Homogeneity of the reaction mixture (for the higher alcohols) was achieved via dropwise introduction of water and intensive mixing. The speed of hydration of vinylacetylene diminished with increasing molecular weight of the alcohol. Hydration proceeded more readily with primary alcohols than with secondary. When vinylacetylene was passed at such a rate that it was completely absorbed by the reaction mixture, then a quantity of alcohol in excess of the equivalent quantity did not substantially influence the yield of hydration product. The total yield of methyl-β-alkoxyethyl ketones was 55-90% of theoretical, calculating on the basis of the quantity of vinylacetylene passed.

All the methyl-β-alkoxyethyl ketones were colorless liquids, with a pleasant fruity odor that distilled without decomposition, and were exceedingly soluble in organic solvents.

The constants of the methyl-β-alkoxyethyl ketones and their 2,4-dinitrophenylhydrazones are set forth in the table. The methyl-β-alkoxyethyl ketones prepared, similarly to other β-alkoxyketones [1], readily condensed

No.	$CH_3COCH_2CH_2OR$	B.p. at 676 mm	n_D^{20}	d_4^{20}	Yield (in %)	M.p. of the 2,4-dinitrophenylhydrazone
1	$R=CH_3$	134-135°	1.4048	0.9235	90	85- 86° [5]
2	$R=C_2H_5$	147-148	1.4117	0.9016	81	100-101
3	$R=C_3H_7$-iso	156-157	1.4092	0.8847	63	220-221
4	$R=C_3H_7$	163-164	1.4145	0.9058	73	87- 89
5	$R=CH_2CH=CH_2$	167-168	1.4300	0.9513	70	212-213.5
6	$R=C_4H_9$-iso	172-173	1.4130	0.8763	61	214-215
7	$R=C_4H_9$	180-181	1.4218	0.8893	70	211-212
8	$R=C_5H_{11}$-iso	190-192	1.4192	0.8781	60	188-190
9	$R=C_6H_{11}$	224-226	1.4585	0.9676	55	217-219
10	$R=C_8H_{17}$	244-246	1.4325	0.8833	59	217-218

with secondary amines to give methyl-β-dialkylaminoethyl ketones:



$$CH_3COCH_2CH_2OR + HN\begin{matrix}R'\\R'\end{matrix} \longrightarrow CH_3COCH_2CH_2N\begin{matrix}R'\\R''\end{matrix}$$

EXPERIMENTAL

Methyl-β-methoxyethyl ketone.

In a three-necked flask supplied with a mercury seal, a reflux condenser, a dropping funnel, a tube for passing in vinylacetylene and a thermometer, 600 g of methanol, 5 g of mercury sulfate and 4 g of sulfuric acid were mixed. The reflux end of the condenser was joined to a Tishchenko bottle containing water. The rate of adding vinylacetylene was controlled by the Tishchenko bottle so that it would be completely absorbed by the reaction mixture In the course of 12 hours, 175 g of vinylacetylene was passed into the reaction mixture, and 200 ml of water was introduced dropwise, and, in five separate portions, 20 g of mercury sulfate was added. After finishing the addition of the vinylacetylene, the reaction mass was thoroughly mixed for one additional hour.

The reaction mixture was then neutralized with soda and the hydration product was extracted with ether. The ether extract was dried with sodium sulfate, and the residue after distilling off the ether was vacuum distilled. 310 g of methyl-β-methoxyethyl ketone with a b.p. 48-50° at 18 mm was collected.

The 2,4-dinitrophenylhydrazone melted at 85-86° (from alcohol).

Methyl-β-ethoxyethyl ketone.

141 g of vinyl acetylene was passed for 16 hours into a boiling mixture of 300 g of ethyl alcohol (99%), 5 g of mercury sulfate, and 4 g of sulfuric acid In addition, 130 g of water was added in drops and 50 additional g of mercury sulfate was added fractionally. Further procedures were carried on exactly as described above. 255 g of methyl-β-ethoxyethyl ketone with a b.p. 67-70° at 35 mm was obtained.

MR_D 32.02; calculated, 31.56.

0.1028 g substance: 0.2327 g CO_2; 0.0962 g H_2O. 0.1000 g substance: 0.2279 g CO_2; 0.0940 g H_2O. Found %: C 61.73, 62.15; H 10.39, 10.44. $C_6H_{12}O_2$. Calculated %: C 62.07; H 10.34.

The 2,4-dinitrophenylhydrazone melted at 100-101° (from alcohol).

Methyl-β-isopropoxyethyl ketone.

Into a boiling mixture of 120 g of isopropyl alcohol, 3 g of sulfuric acid and 2 g of mercury sulfate, 55 g of vinylacetylene was passed over a period of 8 hours. In addition, 45 g of water was added, and 2 g of mercury sulfate was introduced in portions. Further procedures were analogous to the preceeding. 88 g of methyl-β-isopropoxyethyl ketone with a b.p. of 65-67° at 30 mm was obtained.

MR_D 36.45; calculated 36.19.

0.1006 g substance: 0.2378 g CO_2; 0.0974 g H_2O. 0.1032 g substance: 0.2441 g CO_2; 0.1014 g H_2O. Found %: C 64.46, 64.50; H 10.75, 10.91. $C_7H_{14}O_2$. Calculated %: C 64.53; H 10.83.

The 2,4-dinitrophenylhydrazone melted at 220-221° (from acetone).

Methyl-β-propoxyethyl ketone.

Into a boiling mixture of 110 g of propyl alcohol, 2 g of sulfuric acid and 2 g of mercury sulfate, 44.2 g of vinylacetylene was passed, and 60 ml of water and 11 g of mercury sulfate were introduced over a period of 6 hours. Further procedures were conducted as described above. 80 g of methyl-β-propoxyethyl ketone with a b.p. 69-70° at 19 mm was obtained.

MR_D 35.98; calculated 36.19.

0.1023 g substance: 0.2389 g CO_2; 0.0980 g H_2O. Found %: C 63.70; H 10.64. $C_7H_{14}O_2$. Calculated %: C 64.53; H 10.83.

The 2,4-dinitrophenylhydrazone melted at 87-89° (from alcohol).

Methyl-β-allylhydroxyethyl ketone

Into a boiling mixture of 70 g of allyl alcohol and 3 g of mercury sulfate, 40 g of vinylacetylene was passed, 30 ml of water and 10 g of mercury sulfate were introduced over a period of 4 hours. 68 g of methyl-β-allylhydroxyethyl ketone with a b p. of 64-65° at 12 mm was obtained.

MR_D 35.70; **calculated** 35.71.

0.1027 g substance: 0.2458 g CO_2; 0.8513 g H_2O. Found %: C 65.31; H 9.21. $C_7H_{12}O_2$. Calculated %: C 65.52; H 9.43.

The 2,4-dinitrophenylhydrazone melted at 212-213.5° (from acetone).

Methyl-β-isobutoxyethyl ketone.

Into a boiling mixture of 150 g of isobutyl alcohol, 30 g of 20% sulfuric acid and 2 g of mercury sulfate, 48 g of vinylacetylene was passed and 30 ml of water, and 10 g of mercury sulfate were introduced over a period of 5 hours. 80 g of methyl-β-isobutoxyethyl ketone with a b.p. of 64-65° at 11 mm was obtained.

MR_D 41.3; calculated 40.8.

0.1040 g substance: 0.2538 g CO_2; 0.1032 g H_2O. 0.1030 g substance: 0.2522 g CO_2; 0.1032 g H_2O. Found %: C 66.55, 66.77; H 11.12, 11.13. $C_8H_{16}O_2$. Calculated %: C 66.66; H 11.11.

The 2,4-dinitrophenylhydrazone melted at 214-215° (from acetone).

Methyl-β-butoxyethyl ketone.

Into a boiling mixture of 840 g of butyl alcohol, 10 g of sulfuric acid and 5 g of mercury sulfate, 282 g of vinylacetylene was passed with uninterrupted mixing for a duration of 20 hours. 200 ml of water and, in small portions, 40 additional g of mercury sulfate were simultaneously introduced. 547 g of methyl-β-butoxyethyl ketone with a b.p. of 87-89° at 20 mm was obtained.

MR_D 41.14; calculated 40.8.

0.0942 g substance: 0.2306 g CO_2; 0.0966 g H_2O. 0.1047 g substance: 0.2546 g CO_2; 0.1074 g H_2O. Found %: C 66.75, 66.31; H 11.39, 11.39. $C_8H_{16}O_2$. Calculated %: C 66.66; H 11.11.

The 2,4-dinitrophenylhydrazone melted at 211-212° (from acetone).

Methyl-β-isoamylhydroxyethyl ketone

Into a boiling mixture of 430 g of isoamyl alcohol, 50 g of 15% sulfuric acid and 3 g of mercury sulfate, 136 g of vinylacetylene was passed; 90 ml of water and 15 g of mercury sulfate were introduced over a period of 10 hours. 250 g of methyl-β-isoamylhydroxyethyl ketone with a b.p. of 81-82° at 11 mm was obtained.

MR_D 45.52; calculated 45.41.

0.1034 g substance: 0.2604 g CO_2; 0.1099 g H_2O. 0.1037 g substance: 0.2595 g CO_2; 0.1072 g H_2O. Found %: C 68.68, 68.26; H 11.71, 11.48. $C_9H_{18}O_2$. Calculated %: C 68.32; H 11.47.

The 2,4-dinitrophenylhydrazone melted at 188-190° (from acetone).

Methyl-β-cyclohexohydroxyethyl ketone

Into a boiling mixture of 150 g of cyclohexanol, 30 g of 10% sulfuric acid and 3 g of mercury sulfate, 44 g of vinylacetylene was passed, and 50 ml of water and 10 g of mercury sulfate were added over a period of 6 hours. 78 g of methyl-β-cyclohexohydroxyethyl ketone with a b.p. of 111-112° at 16 mm was obtained.

MR_D 48.03; calculated 47.83.

0.1045 g substance: 0.2681 g CO_2; 0.1006 g H_2O. Found %: C 69.97; H 10.69. $C_{10}H_{18}O_2$. Calculated %: C 70.54; H 10.66.

The 2,4-dinitrophenylhydrazone melted at 217-219° (from mixed acetone and methanol).

Methyl-β-octohydroxyethyl ketone

Into a boiling mixture of 80 g of octyl alcohol, 15 g of 15% sulfuric acid and 2 g mercury sulfate, 31 g of vinylacetylene was passed, 30 ml of water and 8 g of mercury sulfate were added over a period of 4 hours. 70 g of methyl-β-octohydroxyethyl ketone with a b.p. of 127-128° at 11 mm was obtained.

MR_D 58.85; calculated 59.27.

0.1034 g substance: 0.2715 g CO_2; 0.1134 g H_2O. 0.0944 g substance: 0.2480 g CO_2; 0.1024 g H_2O. Found %: C 71.61, 71.64; H 12.18, 12.05. $C_{12}H_{24}O_2$. Calculated %: C 71.97; H 12.04.

The 2,4-dinitrophenylhydrazone melted at 217-218° (from acetone).

The Action of Dimethylamine on Methyl-β-isobutoxyethyl ketone.

A mixture of 15 g of methyl-β-isobutoxyethyl ketone (b.p. 172-173° at 676 mm; n_D^{20} 1.4130) and 28 ml of aqueous dimethylamine (30%) in a sealed ampoule was heated on a boiling water bath to the disappearance of the oily layer. The reaction product was neutralized with hydrochloric acid (1:2), after which the neutral substance was extracted with ether. The free base was separated from the aqueous solution with potash, extracted with ether, dried with magnesium sulfate and vacuum distilled. 9 g of methyl-β-dimethylaminoethyl ketone with a b.p. of 65-68° at 22 mm was obtained.

n_D^{20} 1.4320.

The picrate melted at 107° (from water), failed to give a melting point depression in the well-known fashion [6].

Isobutyl alcohol with a b.p. of 105-108° was separated from the ether solution of neutral substances.

SUMMARY

1. It was shown that in alcoholic solutions vinylacetylene is readily hydrated into the corresponding methyl-β-alkoxyethyl ketones.

2. It was established that by increasing the molecular weight of the alcohol, the yield of methyl-β-alkoxyethyl ketones is diminished. A quantity of alcohol in excess of the equivalent amount did not substantially influence the yield of hydration product.

3. Methyl-β-alkoxyethyl ketones are readily condensed with secondary amines with the formation of methyl-β-dialkylaminoethyl ketones.

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THE ACTION OF PRIMARY AND SECONDARY AMINES ON TETRAHYDRO-4-PYRONES

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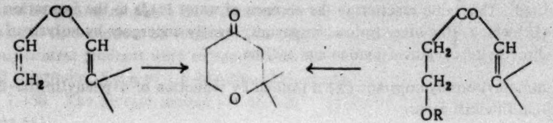
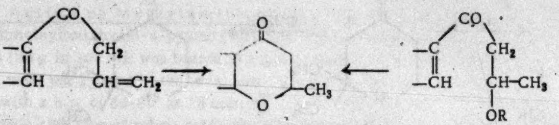
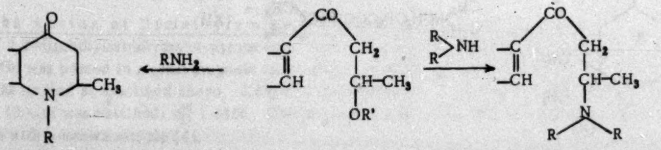
Methods were described in our previous works for preparing tetrahydro-4-pyrones via the hydration of divinyl ketones [1] and vinylallyl ketones [2] or by way of the hydrolysis of the corresponding β-alkoxy ketones.





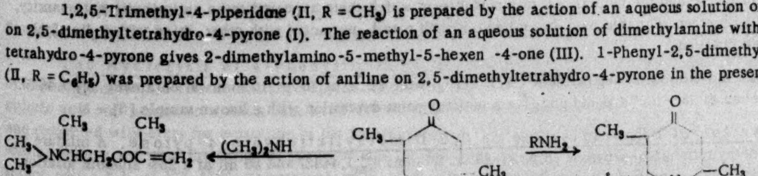
It was also well known that the alkoxyl group in β-alkoxy ketones is readily split off under the influence of primary amines with formation of 4-piperidones [3]. β-Dialkylamino ketones are obtained in excellent yield by the action on β-alkoxy ketones of secondary amines [4]:



It was of interest to examine the possibility of cleavage of tetrahydro-4-pyrones by primary and secondary amines.

The study of this reaction established that the tetrahydropyrone ring is readily split by the action of aqueous solutions of primary and secondary amines on tetrahydro-4-pyrones at 60-70°, with the formation of the corresponding 4-piperidones and β-dialkylamino ketones.

1,2,5-Trimethyl-4-piperidone (II, R = CH_3) is prepared by the action of an aqueous solution of methylamine on 2,5-dimethyltetrahydro-4-pyrone (I). The reaction of an aqueous solution of dimethylamine with 2,5-dimethyltetrahydro-4-pyrone gives 2-dimethylamino-5-methyl-5-hexen-4-one (III). 1-Phenyl-2,5-dimethyl-4-piperidone (II, R = C_6H_5) was prepared by the action of aniline on 2,5-dimethyltetrahydro-4-pyrone in the presence of water.

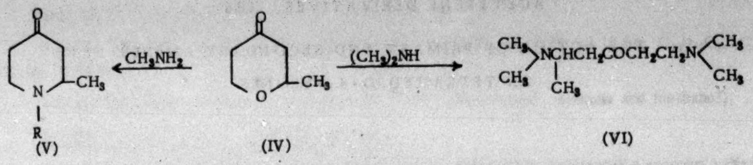


$(CH_3)_2NCH(CH_3)CH_2COC(CH_3){=}CH_2$

R = CH_3, C_6H_5

The reaction with 2-methyltetrahydro-4-pyrone (IV) proceeds in an analogous manner.

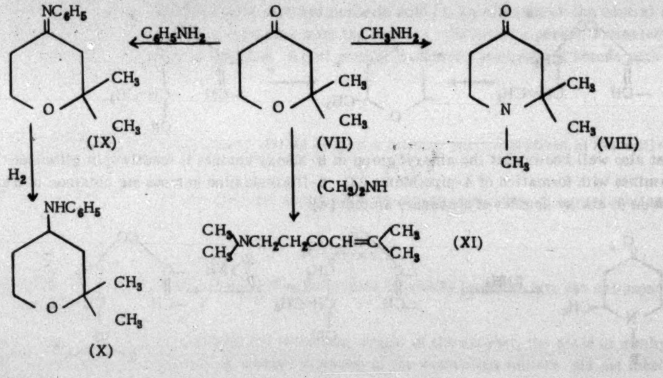
By the action of an aqueous solution of methylamine on this ketone, 1,2-dimethyl-4-piperidone (V) is formed, while the action of an aqueous solution of dimethylamine gave 1,5-bis-dimethylaminohexan -3-one (VI).



The reaction of an aqueous solution of dimethylamine with 2,2-dimethyltetrahydro-4-pyrone (VII) leads to the formation of 1-dimethylamino-5-methyl-4-hexen-3-one (XI), while the action of an aqueous solution of methylamine on this same ketone forms 1,2,2-trimethyl-4-piperidone which, however, is strongly resinified in the reaction process.

The reaction product resulting from the action of aniline on 2,2-dimethyltetrahydro-4-pyrone in the presence of water is completely resinified. This same reaction in the absence of water leads to the formation in good yield of a 4-phenylimino derivative (IX) which, like other imino compounds, readily undergoes hydrolysis in acidic media with formation of the initial 2,2-dimethyltetrahydro-4-pyrone and aniline.

4-Phenylamino-2,2-dimethyltetrahydropyran (X) is formed by reduction of 4-phenylimino-2,2-dimethyltetrahydropyrane (IX) by sodium in moist ether:



EXPERIMENTAL

The Action of Methylamine on 2,5-Dimethyltetrahydro-4-pyrone. A mixture of 7 g of 2,5-dimethyltetrahydro-4-pyrone (I) (b.p. 87-89° at 30 mm; n_D^{20} 1.4483) and 14 ml of a 24% aqueous solution of methylamine was heated in a glass ampoule on a water bath at 60-70° for 5 hours. Excess methylamine was distilled off on a water bath at 50° in a 70 mm vacuum. The solution was acidified with hydrochloric acid to a weakly acidic reaction, and the neutral reaction products, of which there appeared to be an insignificant quantity, were extracted with ether. Organic base was salted out with potash, extracted with ether, dried with sodium sulfate and vacuum distilled.

3.5 g of 1,2,5-trimethyl-4-piperidone (II, R = CH_3) with a b.p. of 78° at 10 mm was obtained; n_D^{20} 1.4610. The picrate melted at 161-162° and did not give a melting point depression with a known sample [3].

The Action of Dimethylamine on 2,5-Dimethyltetrahydro-4-pyrone. A mixture of 10 g of 2,5-dimethyltetrahydro-4-pyrone (b.p. 87-89° at 30 mm; n_D^{20} 1.4483) and 50 ml of a 25% aqueous solution of dimethylamine was heated in a glass ampoule on a water bath at 60-70° for 4 hours. Excess dimethylamine was vacuum distilled off on a water bath. The reaction product was acidified with hydrochloric acid (1: 3), and neutral substances were extracted with ether. Organic base was salted out with potash, extracted with ether, dried with sodium sulfate and vacuum distilled. 6 g of 2-dimethylamino-5-methyl-5-hexen-4-one (III) with a b.p. of

77-80° at 6 mm was obtained; n_D^{20} 1.4560. The picrate melted at 124-125° and failed to give a melting point depression with a known sample [4].

The Action of Aniline on 2,5-Dimethyltetrahydro-4-pyrone. A mixture of 10 g of 2,5-dimethyltetrahydro-4-pyrone (b.p. 169-171°, n_D^{20} 1.4480), 10 g of aniline and 5 ml of water was heated with a reflux condenser on a metallic bath at 130-140° for 8 hours. After the heating was ended, the reaction mixture was vacuum distilled. 4 g of 1-phenyl-2,5-dimethyl-4-piperidone (II, $R = C_6H_5$) with b.p. 116-118° at 1.5 mm was obtained; n_D^{20} 1.5520. The hydrochloride melted at 157-158° and failed to give a melting point depression with a known sample [5].

The Action of Methylamine on 2-Methyltetrahydro-4-pyrone. A mixture of 10 g of 2-methyltetrahydro-4-pyrone (IV) (b.p. 168-169°, n_D^{20} 1.4440) and 20 ml of an aqueous solution of methylamine (24%) was heated in a glass ampoule at 50-60° for a duration of 4 hours. Excess methylamine was distilled off on a water bath at 50° in a vacuum of 70 mm. The reaction product was acidified with hydrochloric acid (1:2) to eliminate the neutral substances and treated as indicated above. 2.3 g of 1,2-dimethyl-4-piperidone (V) with a b.p. of 80-82° at 10 mm was obtained; n_D^{20} 1.4583. The picrate melted at 163-164° (alcohol) and failed to give a melting point depression with a known sample [3].

The Action of Dimethylamine on 2-Methyltetrahydro-4-pyrone. A mixture of 12 g of 2-methyltetrahydro-4-pyrone (b.p. 168-189°; n_D^{20} 1.4440) and 25 ml of an aqueous solution of dimethylamine (25%) was heated in a glass ampoule for a duration of 4 hours at 60-70°. Excess dimethylamine was distilled off on a water bath at 50° in a vacuum of 70 mm. The solution was acidified with added hydrochloric acid to a weakly acidic reaction, neutral products were extracted with ether, these appeared to be present in insignificant quantity. After the usual treatment, 5.2 g of 1,5-bis-dimethylaminohexan-3-one (VI) with a b.p. of 84-86° at 9 mm was obtained; n_D^{20} 1.456. The picrate melted at 145-146° (alcohol) and failed to give a melting point depression with a known sample [4].

The Action of Methylamine on 2,2-Dimethyltetrahydro-4-pyrone. A mixture of 15 g of 2,2-dimethyltetrahydro-4-pyrone (VII) (b.p. 178-179°; n_D^{20} 1.4465) and 30 ml of an aqueous solution of methylamine (25 g in 100 ml) was heated in a glass ampoule on a water bath at 60-70° for a duration of 4 hours. The reaction mass was treated in the usual way. 2.5 g of a liquid that quickly darkened in air and had the odor of an amine with a b.p. of 60-63° at 13 mm; n_D^{20} 1.4500, was obtained. On mixing this fraction with a saturated solution of picric acid (2 g of picric acid), the picrate immediately precipitated. After recrystallization from alcohol, 2.8 g of the picrate of 1,2,2-trimethyl-4-piperidone (VIII) with a m.p. of 138.5-139.5° was obtained.

0.1002 g substance: 15.0 ml N_2 (17°, 673 mm). 0.1002 g substance: 15.2 ml N_2 (16.5°, 672 mm). Found %: N 15.59, 15.77. $C_{14}H_{18}O_8N_4$. Calculated %: N 15.13.

The Action of Dimethylamine on 2,2-Dimethyltetrahydro-4-pyrone. A mixture of 10 g of 2,2-dimethyltetrahydro-4-pyrone (b.p. 178-179°; n_D^{20} 1.4465) and 40 ml of an aqueous solution of dimethylamine (24%) was heated in a glass ampoule on a water bath at 60-70° for a duration of four hours. The reaction product was treated as described above. 5.8 g of 1-dimethylamino-5-methyl-4-hexen-3-one (XI) with a b.p. 83-85° at 13 mm was obtained; n_D^{20} 1.4600. The picrate melted at 106-107° and failed to give a melting point depression with a known sample [4].

The Action of Aniline on 2,2-Dimethyltetrahydro-4-pyrone. A mixture of 28 g of 2,2-dimethyltetrahydro-4-pyrone (b.p. 178-179°; n_D^{20} 1.4465) and 30 g of aniline was heated on a metallic bath at 150-160° for 8 hours, after which the reaction mass was vacuum distilled. 2.2 g of 4-phenylimino-2,2-dimethyltetrahydropyrane (IX) with a b.p. of 109-110° at 2 mm was collected.

n_D^{20} 1.5413; d_4^{20} 1.0360; MR_D 61.65; calculated 60.92.

0.1031 g substance: 0.2894 g CO_2; 0.0788 g H_2O. 0.0952 g substance: 0.2671 g CO_2; 0.0753 g H_2O. Found %: C 76.55, 76.51; H 8.49, 8.72. $C_{13}H_{17}ON$. Calculated %: C 76.88; H 8.42.

The Hydrolysis of 4-Phenylimino-2,2-dimethyltetrahydropyran. A solution of 15 g of 4-phenylimino-2,2-dimethyltetrahydropyran (IX) (b.p. 109-110° at 2 mm; n_D^{20} 1.5413) in 50 ml of 16% hydrochloric acid was heated on a water bath at 50° for 2 hours. The reaction mixture was saturated with sodium chloride and extracted with ether for separation of the neutral products of hydrolysis. The ether extract was dried with with sodium sulfate and after distilling off the ether, the residue was distilled at atmospheric pressure. 4.5 g of a substance with a b.p. of 177-179° was obtained; n_D^{20} 1.4463. The semicarbazone melted at 164-165° and failed to give a melting point depression with a known sample of the semicarbazone of 2,2-dimethyltetrahydro-4-pyrone [1].

The aqueous solution, after separation of the ethereal layer, was treated with excess alkali, and the oil which separated was extracted with ether, dried with sodium sulfate and was distilled at atmospheric pressure. 3 g of a substance with a b.p. of 179-182° was obtained. The hydrochloride melted at 198-200° and failed to give a melting point depression with aniline hydrochloride.

Reduction of 4-Phenylimino-2,2-dimethyltetrahydropyran by Sodium in Moist Ether. A mixture of 15 g of 4-phenylimino-2,2-dimethyltetrahydropyran (IX) (b.p. 109-110° at 2 mm; n_D^{20} 1.5413), 30 ml of water and 150 ml of ether was mixed in a three-necked flask, supplied with a stirrer, a mercury seal and a condenser. While the flask was constantly stirred, 15 g of finely divided metallic sodium was introduced in such a manner that the ether continued to boil regularly. After complete solution of the sodium, 30 ml of water was added to the reaction mass. The ether layer was separated and dried with sodium sulfate. After the ether was distilled off, the hard residue was recrystallized from a mixture of benzene and alcohol. 10 g of 4-phenylamino-2,2-dimethyltetrahydropyran (X) with a b.p. of 98-99° was obtained.

0,1024 g substance: 0.2872 g CO_2; 0.0903 g H_2O. 0.1002 g substance: 0.2810 g CO_2; 0,0896 g H_2O. Found %: C 76,49, 76.48; H 9.79, 9.93. $C_{13}H_{19}ON$. Calculated %: C 76.14, H 9,33.

The hydrochloride of 4-phenylamino-2,2-dimethyltetrahydropyran was prepared by the action of hydrogen chloride on a solution of the base in absolute ether. After having been reprecipitated from the alcoholic solution by absolute ether, it melted at 164.5-165.5°.

SUMMARY

1. It was shown that by the action of aqueous solutions of primary and secondary amines on tetrahydro-4-pyrones, the heterocyclic ring is readily cleaved at the oxygen atom with formation of the corresponding 4-piperidones and β-dialkylamino ketones.

2. It was shown that by the action of aniline on 2,2-dimethyltetrahydro-4-pyrone in the absence of water, only 4-phenylimino-2,2-dimethyltetrahydropyran is formed.

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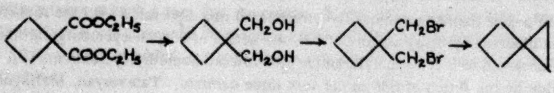
* See Consultants Bureau Translation, page 1833.

** See Consultants Bureau Translation, page 923.

SPIROHEXANE

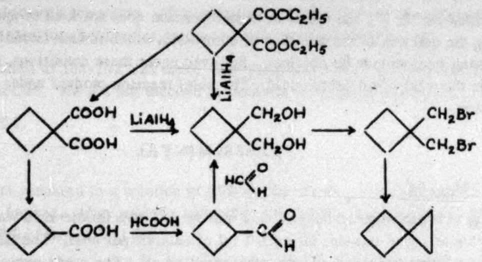
Ya. M. Slobodin and M. V. Blinova

In 1913 the first attempt to synthesize spirohexane was made by Zelinsky and Uedinov [1] according to the scheme



A Bouveault and Blanc reduction of the ester of cyclobutanedicarboxylic acid led to such a low yield of 1,1-dimethylolcyclobutane that the authors were not able to carry the work to a conclusion. There were no other attempts to synthesize this hydrocarbon.

The possibility of synthesizing spirohexane according to the diagram below was studied in the present investigation.



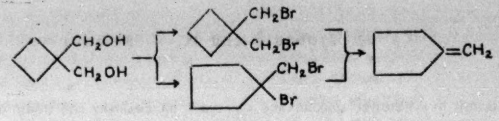
Reduction of the ester of cyclobutanedicarboxylic acid with lithium-aluminum hydride led to an insignificant yield of the diol. Better yields of the diol were obtained by lithium-aluminum hydride reduction of the cyclobutanedicarboxylic acid itself, but they were all low, not exceeding 25-30%. According to the third of the methods used, cyclobutanedicarboxylic acid was converted to cyclobutanecarboxylic acid. By passing a mixture of cyclobutanecarboxylic and formic acids in molar proportions of 1:3 over an MnO catalyst at 400°, cyclobutylformaldehyde was obtained with a yield of 47% of the theoretical. Dimethylolcyclobutane in a yield of 70% was obtained by condensation of this aldehyde with formaldehyde in an alkaline medium.

The diol obtained by reduction with lithium-aluminum hydride was a crystalline substance with a melting point of 138-139°, while the diol prepared by condensation of cyclobutylformaldehyde with formaldehyde did not crystallize. The diols did not differ in the rest of their properties.

The dibromide was obtained by the action of PBr_3 on the diol. The hydrocarbon was obtained by splitting off bromine from the dibromide by the use of zinc powder in alcohol.

Intense lines with a frequency of 1659 cm^{-1} were detected in the Raman spectrum of the hydrocarbon, which indicated the presence in it of double bonds. Hydrogenation over a platinum catalyst established that the hydrocarbon added hydrogen in a quantity corresponding to one double bond. Cyclopentanone and formic acid were fomed by ozonolysis. These data confirm a methylenecyclopentane structure for the hydrocarbon. The physical properties of the hydrocarbon also corresponded with the properties of methylenecyclopentane.

Formation of methylenecyclopentane appears to be the result of a rearrangement which, in our synthesis, may occur either in the stage of preparation of the bromide from dimethylolcyclobutane under the influence of PBr_3, or in the stage of formation of the hydrocarbon under the influence of $ZnBr_2$



Expansion of a four-membered into a five-membered ring associated with the replacement of a hydroxyl by a halogen has been observed by many authors. Thus, the action of PBr_3 on cyclobutylcarbinol yielded a mixture of bromides which contained 56% cyclopentylbromide and 44% bromomethylcyclobutane [2]. Demyanov [3] obtained cyclopentylbromide by the action of HBr on the very same carbinol. Tatevosyan, Melikyan and Terzyan [4] obtained methylcyclopentylbromide by the action of HBr on methylcyclobutylcarbinol. Kizhner [5] in the course of a study of the reaction of HBr and HI on tertiary alcohols containing the cyclobutyl radical established that halogen derivatives of the cyclopentane series are obtained as a result of the reaction. T. Favorsky and Yakovlev [6] showed that tertiary alcohols containing the cyclobutyl radical form a mixture containing compounds both of the cyclobutane series and of the cyclopentane series on reaction with HCl.

The data we have obtained show a great similarity between the synthesis of spirohexane studied by us and the synthesis of the simplest spirane – spiropentane.

As was demonstrated earlier [7], the synthesis of spiropentane does not lead to appreciable yields of spirane, and only by conducting the reaction in the presence of compounds which reduce isomeric transformation can a hydrocarbon mixture containing spiropentane be obtained. But even under these conditions, the yield of spiropentane is considerably lower than the total hydrocarbon yield. The chief reaction product under all circumstances appears to be methylenecyclobutane.

EXPERIMENTAL

Cyclobutylformaldehyde

A mixture of 50 g of cyclobutanecarboxylic acid and 82 g of 84% formic acid was passed at 410-420° through a tube with MnO at a rate of 1 g of mixture for each 1 ml of catalyst per hour. The reaction product was extracted with ether, the ethereal solution was dried and the ether distilled off. The crude cyclobutylformaldehyde boiled at 85-120°. The yield of aldehyde was 15.5 g. The recovery of unreacted cyclobutanecarboxylic acid was 18 g. On repeated distillation, the aldehyde boiled at 113-115° [8]; d_4^{20} 0.9355; n_D^{20} 1.4357; MR_D 23.47; calculated 23.56. Found %: C 71.21; H 9.69. C_5H_8O. Calculated %: C 71.43; H 9.52. 2,4-Dinitrophenylhydrazone m.p. 153-154°; Found %: N 21.53. Calculated %: N 21.21.

Raman spectrum

325 (1), 463 (2), 606 (1), 759 (1), 871 (3), 924 (8), 958 (8), 1020 (7), 1055 (2), 1088 (1), 1118 (1), 1158 (2), 1184 (1), 1218 (2), 1247 (0.5), 1331 (2), 1385 (7), 1445 (10), 1470 (1), 1716 (10), 2865 (3), 2914, 2947, 2975.

Cyclobutylformaldehyde polymerized very readily under the influence of calcium chloride. After crystallization from ether the polymer consisted of small white needles with a melting point of 118.5-120.5°. Found: M 254. $(C_5H_8O)_3$. Calculated: M 252.

1,1-Dimethylolcyclobutane

1) In a flask equipped with a stirrer, a reflux condenser and two dropping funnels, were mixed 34 g of 34% formaldehyde and 123 ml of water. In the course of 3 hours' intensive stirring, there were simultaneously added a suspension of 8.3 g of calcium hydroxide in 47 ml of water from one dropping funnel and 15.5 g of cyclobutylformaldehyde at 30° from the other. After addition of the reactants, the mixture was heated at 50° for one hour. The $Ca(OH)_2$ precipitate was filtered off after cooling. The solution was neutralized by the addition of sulfuric acid. The water was vacuum-distilled off. The concentrated solution was filtered from the salt precipitate and the diol extracted with dichloroethane for a duration of 7-10 days. After the solvent was distilled off, the diol was redistilled in a vacuum. The yield of product with a b.p. of 134-140° at 15 mm was 70% of theoretical. After repeated redistillation, the diol boiled at 134-136° at 15 mm [1].

d_4^{20} 1.0675; n_D^{20} 1.4754; MR_D 30.62; calculated 31.22. Found %: C 62.75; H 10.28. $C_6H_{12}O_2$. Calculated %: C 62.07; H 10.34.

2) An ethereal solution of the ester of cyclobutanedicarboxylic acid was added to a solution of lithium-aluminum hydride in absolute ether at such a rate that the mixture boiled mildly. Upon completion of the addition, the mixture was stirred for 1.5 hours more after which it was carefully decomposed with water and then acidified by the addition of sulfuric acid. The aqueous solution was extracted with ether, the ethereal solution dried over potash and the ether distilled off. Almost the entire product redistilled at 119-121° (23 mm). Its properties showed it to be the starting cyclobutanedicarboxylic acid. The diol was isolated in insignificant quantity.

3) To an ethereal solution of lithium-aluminum hydride prepared from 10 g of lithium hydride and 39 g of freshly prepared aluminum chloride, a solution of 15 g of cyclobutanedicarboxylic acid in 200 ~~ml~~ of absolute ether was added with energetic mixing at such a rate that the contents of the flask boiled weakly. On completion of the addition of the acid, the mixture was stirred for 20 minutes more and then the flask containing the mixture was cooled with ice water and 30 ml of water was added in drops. The ethereal solution was poured off from the $Al(OH)_3$ precipitate, dried, and redistilled.

The diol redistilled at 143-145° (24 mm). It was a glycerin-like liquid which crystallized on standing. After recrystallization from dichloroethane, the diol consisted of white silky crystals with a m.p. of 138-139°.

0.1232 g sub.: 0.2794 g CO_2; 0.1143 g H_2O. Found %: C 61.93; H 10.30. $C_6H_{12}O_2$. Calculated %: C 62.07; H 10.34.

1,1-Dibromodimethylcyclobutane

20% by weight of pyridine was added to the diol to prepare the bromide. The mixture was slowly added to PBr_3 placed in a flask cooled with ice water. After addition of all the diol the mixture was heated to 60-80°. The reaction product was decanted into cold water, extracted with ether and redistilled.

The bromide redistilled at 102-104° (23 mm). The yield was 40% of theoretical. The bromide quickly darkened and split off hydrogen bromide. We did not succeed in isolating it in the pure form.

d_4^{20} 1.5786; n_D^{20} 1.5260.

Hydrocarbon

The hydrocarbon was prepared in a solution of 85% alcohol by the action of zinc powder on the dibromide and was distilled off as it was formed. After washing with water the hydrocarbon was dried and redistilled over metallic sodium. The yield was 76% of theoretical [9].

b.p. 72-75°; d_4^{20} 0.7859; n_D^{20} 1.4321; MR_D 27.06. C_6H_{10}. Calculated: MR_D 27.24.

Raman spectrum:

366 (2 w), 412 (1), 538 (4), 578 (2), 683 (1), 723 (1), 772 (2), 850 (2), 889 (4), 923 (1), 957 (1), 986 (6 w), 1024 (1), 1101 (1), 1177 (1), 1220 (0.5), 1412 (2), 1449 (2), 1453 (2), 1623 (1), 1659 (6), 2101 (1), 2872 (4), 2944 (4).

0.1865 g of hydrocarbon underwent hydrogenation. The absorption of hydrogen was 57.4 ml (19°, 754 mm) or 104.6% of that calculated on the basis of the molecular formula C_6H_{10} with one double bond.

Ozonolysis of the hydrocarbon. 1 g of the hydrocarbon was dissolved in 15 ml of ethyl chloride. Ozonolysis was conducted with the mixture cooled to −70°. The ozonide was unstable and decomposed on contact with moist air. After decomposition of the ozonide with water, the general acidity was determined by titrating with KOH. The acid content was 0.266 g. The content of formic acid determined by the calomel method was 0.232 g.

The neutral products of the decomposed ozonide were extracted with ether from the alkaline solution and the ether distilled off. The 2,4-dinitrophenylhydrazone melted at 140-142° after one recrystallization from alcohol. A test mixture with 2,4-dinitrophenylhydrazone prepared from cyclopentanone melted without depression.

SUMMARY

1. Cyclobutylformaldehyde was prepared by passing a mixture of cyclobutanecarboxylic and formic acids over MnO at 410-420°.

2. 1,1-Dimethylolcyclobutane was prepared by the condensation of cyclobutylformaldehyde with formaldehyde in an alkaline medium and also by reduction of cyclobutanedicarboxylic acid with lithium-aluminum hydride.

3. By the action of zinc powder on 1,1-dibromodimethylcyclobutane under the conditions of the Gustavson reaction, methylenecyclopentane was obtained. Spirohexane was not formed under these conditions.

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* See Consultants Bureau Translation, page 133, 267.

** See Consultants Bureau Translation, page 2231.

*** See Consultants Bureau Translation, page 37.

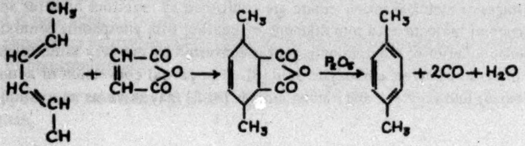
HYDROCARBON SYNTHESIS

XLIII. A NEW REACTION OF TETRAHYDROPHTHALIC ANHYDRIDES (PRODUCTS OF THE DIENE SYNTHESIS) WITH PHOSPHORUS PENTOXIDE

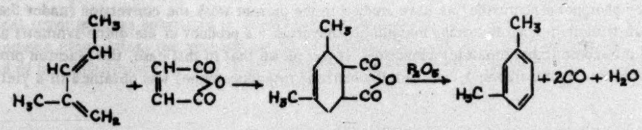
R. Ya. Levina, V. R. Skvarchenko, N. S. Kataeva and E. G. Treshchova

We previously [1] described a new reaction – the conversion under the influence of phosphorus pentoxide of tetrahydrophthalic anhydrides (addition products of the coupling of diene hydrocarbons with maleic anhydride) into aromatic hydrocarbons. The reaction results in the simultaneous dehydrogenation and decarboxylation of the initial tetrahydrophthalic anhydrides.

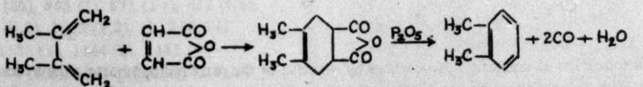
p-Xylene was thus obtained by heating phosphorus pentoxide with 3,6-dimethyl-1,2,3,6-tetrahydrophthalic anhydride (obtained in turn by addition of maleic anhydride to hexadiene-2,4).



The reaction between phosphorus pentoxide and 3,5-dimethyl-1,2,3,6-tetrahydrophthalic anhydride (from 2-methylpentadiene-1,3 and maleic anhydride) led to the production of m-xylene.

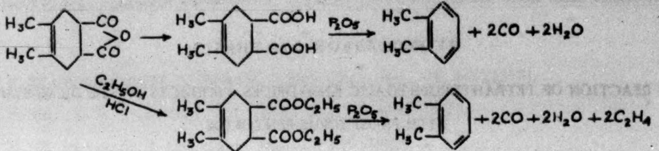


4,5-Dimethyl-1,2,3,6-tetrahydrophthalic anhydride (the addition product of 2,3-dimethylbutadiene-1,3 and maleic anhydride) is converted into o-xylene under the very same conditions.

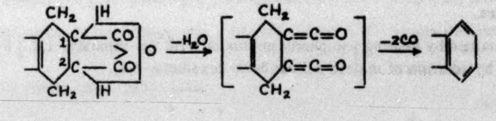


The yields of xylenes were respectively 80, 60 and 40% of the theoretical quantity.

It was further established that not only the anhydrides of the tetrahydrophthalic acid, but also the acids themselves and their esters are similarly cleaved by phosphorus pentoxide, being converted with the loss of water and carbon dioxide (and in the case of the ester, with the splitting off of ethylene) into aromatic hydrocarbons.



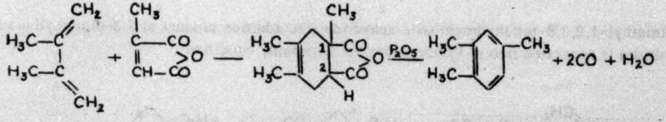
It may be assumed that in the reaction between phosphorus pentoxide and the tetrahydrophthalic anhydrides, dehydrogenation initially proceeds with the formation as intermediate compounds of the corresponding ketenes which thereupon undergo decarboxylation, simultaneous redistribution of hydrogen within the ring, and formation of a stable aromatic ring, for example:



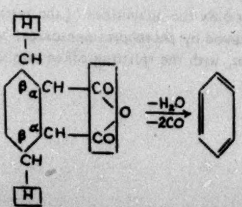
The separate stages of such a reaction course are confirmed by reactions of acids and ketenes. Thus, for example, the conversion of malonic acid into diketene by heating with phosphorus pentoxide is described in the literature [2]; the monoethylester of ethylmalonic acid is converted by the very same reagent into the corresponding ketene derivative – the ester of ketenecarboxylic acid [3]. The partial conversion of ketene (in the course of its preparation from acetone) into ethylene and carbon dioxide [4, 5] may serve as an example of the decarboxylation of ketene.

In this case, if the conversion of the tetrahydrophthalic anhydrides under the influence of phosphorus pentoxide actually passes through a stage of ketene formation, a necessary precondition for this reaction appears to be the presence of hydrogen atoms in the 1 and 2-positions (i.e., in the positions α to the carboxyl groups); the reaction should not take place for tetrahydrophthalic anhydrides with alkyl groups even in one of these positions.

In an attempt to elucidate the mechanism of the conversion of the tetrahydrophthalic anhydrides into aromatic hydrocarbons by phosphorus pentoxide, we have studied in the present work the conversion (under these reaction conditions) of 1,4,5-trimethyl-1,2,3,6-tetrahydrophthalic anhydride – a product of the diene synthesis using 2,3-dimethylbutadiene and citraconic (methylmaleic) anhydride. It was shown that in this case, the reaction proceeds normally with formation of aromatic hydrocarbons; 1,2,4-trimethylbenzene (pseudocumene) was obtained in a yield of 65% of the theoretical.



Thus, the formation of aromatic hydrocarbons by reaction of the tetrahydrophthalic anhydrides or acids with phosphorus pentoxide is linked with the simultaneously proceeding processes of dehydrogenation (of the hydrogen atoms in a β-position relative to the carboxyl groups) and of decarboxylation, and is not associated with intermediate ketene formation.



EXPERIMENTAL

1,4,5-Trimethyl-1,2,3,6-tetrahydrophthalic anhydride was prepared by heating 26 g of 2,3-dimethylbutadiene-1,3 (b.p. 69-70°, n_D^{20} 1.4385) with 35 g of citraconic anhydride (b.p. 95° at 5 mm) in 25 ml of benzene for 9 hours. After distilling off the benzene and vacuum distilling, 19.4 g (33%) of the addition product was obtained:

b.p. 175-177° (2-3 mm); n_D^{20} 1.4780; d_4^{20} 1.1052; MR_D 50.0. $C_{11}H_{14}O_3 \digamma$. Calculated: MR_D 49.79.

The addition product of 2,3-dimethylbutadiene-1,3 and citraconic anhydride (1,4,5-trimethyl-1,2,3,6-tetrahydrophthalic anhydride) had not been described in the literature.

To 19.4 g (0.1 mole) of the trimethyltetrahydrophthalic anhydride stirred in a Würtz flask with a descending condenser, was added 14.4 g (0.1 mole) of phosphorus pentoxide and the mixture was carefully heated to 150° to initiate the reaction, after which heat evolved in the reaction raised the temperature to 200°. The hydrocarbon began to distill off at 290° (in the reaction mass); to complete the reaction the mixture was heated by degrees to 350°. The hydrocarbon obtained was washed with a warm salt solution, with water, 80% sulfuric acid and again with water until the reaction was neutral, dried with calcium chloride and redistilled over sodium.

9 g (65%) of pseudocumene was obtained:

b.p. 168.5° (753 mm); n_D^{20} 1.5030; d_4^{20} 0.8700; MR_D 40.51. $C_9H_{12} \digamma_3$. Calculated: MR_D 40.16.

Literature data for pseudocumene [6]: b.p. 169.18° (760 mm); n_D^{25} 1.5025; d_4^4 0.8762.

The isomers of pseudocumene, mesitylene (1,3-5-trimethylbenzene) and hemimellitene (1,2,3-trimethylbenzene), which might be produced if migration of the methyl groups occurred in the reaction of the starting trimethyltetrahydrophthalic anhydride with phosphorus pentoxide, have constants quite different from the constants of pseudocumene (particularly in the case of hemimellitene).

Mesitylene [7]: b.p. 164.6° (749 mm); n_D^{20} 1.4985; d_4^{20} 0.8639. Hemimellitene [8]: b.p. 175.5° (744 mm); n_D^{20} 1.5132; d_4^{20} 0.8949.

Examination of the Raman spectrum of the hydrocarbon showed that it exhibited frequencies coinciding with those given by Fenske [9] for pseudocumene.

In the table below are arranged the spectrum of the pseudocumene we synthesized and the data given in the literature for this compound. The exposure method and the apparatus were described earlier [10]. The intensities of the spectrum lines are given on a ten-point visual scale.

Our optical investigations permitted us to establish the absence of admixture of misitylene and hemimellitene in the pseudocumene preparation; the very intense lines of mesitylene [9]: 570 (0.555), 995* (0.487), 225 (0.482), 509 (0.304); and of hemimellitene [9]: 652 (0.627), 225 (0.151), 995* (0.129), 480 (0.119), 1092* (0.168) are absent.

TABLE

Raman spectrum of 1,2,4-trimethylbenzene**	
Obtained in the present work	From literature data (Fensky [9])
215 (13 s), 290 (4), **323 (25 s)**, 417 (1), 436 (5), **470 (15)**, 495 (1.5), **556 (35)**, 663 (1), 686 (1.8), **718 (12)**, **746 (50)**, 805 (1), 871 (1 s), 912 (0.6), **927 (10)**, 985 (0.5), 1022 (1.2), 1042 (0.5 s), 1093 (0.5 s), 1130 (3), 1144 (2), 1161 (2), 1192 (1.2), 1212 (1.8), **1247 (30)**, 1268 (1.5), 1296 (2), 1324 (1), 1380 (7), **1383 (10)**, 1443 (3), 1452 (5), 1582 (3), **1621 (10)**.	202 (0.047), 275 (0.022), **314 (0.236)**, 432 (0.064), **465 (0.198)**, 490 (0.024), **549 (0.296)**, 603 (0.013), 686 (0.060), **716 (0.208)**, **741 (0.477)**, 805 (0.017), 871 (0.016), **920 (0.146)**, 1023 (0.031), 1122 (0.043), 1147 (0.035), 1186 (0.023), 1208 (0.040), **1244 (0.336)**, 1325 (0.015), **1378 (0.254)**, 1443 (0.120), 1576 (0.065), **1618 (0.200)**.

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* The line in the region of 990 cm^{-1}, characteristic of mesitylene and hemimellitene and the line 1092 characteristic of hemimellitene, were present in the spectrum of our preparation of pseudocumene but had a very insignificant intensity; in the absence of the other intense lines of mesitylene and hemimellitene these weak spectrum lines can not be ascribed to admixture of these hydrocarbons.

** The Raman spectrum of our pseudocumene preparation was obtained with a slit aperture of 6 cm^{-1}, while Fenske's data were obtained with a slit aperture of 15 cm^{-1}, which evidently explains some discrepancy in the frequency values.

SUMMARY

1. We investigated the mechanism of a reaction developed by us – the conversion into hydrocarbons of tetrahydrophthalic anhydrides (addition products of dienes and maleic anhydride) by the action of phosphorus pentoxide.

2. It was established that this reaction does not include an intermediate stage of formation of a ketene system, i.e., decarboxylation proceeds simultaneously with dehydration in which β-hydrogen atoms (β in relation to the carboxyl groups) participate.

3. By the reaction of phosphorus pentoxide with 1,4,5-trimethyl-1,2,3,6-tetrahydrophthalic anhydride (from 2,3-dimethylbutadiene and citraconic anhydride), 1,2,4-trimethylbenzene (pseudocumene) was obtained in a yield equal to 65% of the theoretical and without admixture of the isomeric trimethylbenzenes.

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THE REDUCING ACTION OF SECONDARY ALKYLMAGNESIUM HALIDES ON ESTERS AND ACID CHLORIDES

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The study of the dependence of the antiknock properties of liquid motor fuel and of its freezing point on the structure of its constitutent hydrocarbons necessarily involves the synthesis of individual hydrocarbons with tertiary and quaternary carbon atoms.

A leading place among the methods of synthesizing branched hydrocarbons is occupied by the organomagnesium synthesis according to the classical scheme of Butlerov, Zaitsev and Grignard. Its application for the synthesis of secondary and tertiary alkylmagnesium halides and carboxyl compounds with radicals which give rise to steric hindrance, leads to an anomalous reaction course.

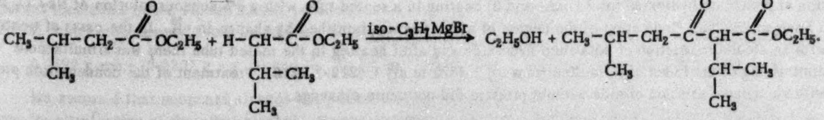
Many investigations have been devoted to the study of the anomalous reaction of secondary and tertiary alkylmagnesium halides with esters and acid chlorides (the works of A. D. Petrova and co-workers, I. I. Lapkina and co-workers, F. Whitmore, and others). It was shown in these investigations that the primary reaction products formed were ketones of the RCOR' and RCOR types (where R is the acid radical and R' the radical of the organomagnesium compound), products of their reduction of the secondary alcohol type, and also products of esterification, condensation and certain other reactions.

The reducing and the condensing actions of isopropylmagnesium bromide in its reaction with the ethyl ester of isovaleric acid were investigated in the first part of the present work.

Investigation of the reaction products showed the presence in the final products synthesized, along with unchanged ester, of about 10% of isopropylisobutyl ketone, 9% of a product of its reduction, isopropylisobutylcarbinol, and 14% of a condensation product which according to the analytical data was ethyl-α-isovalerylisovalerate.

The absence of a tertiary alcohol of the composition RR'_2COH and the presence of a ketone of the RCOR' type in the reaction products indicated that the reaction stopped at the first stage of the normal reaction. The reducing activity of isopropylmagnesium bromide (involved in the isolation of a proportional quantity of propylene [1]) led to the formation of an alcohol of the composition RCHOHR'.

The condensing action of isopropylmagnesium bromide on the starting material —ethyl isovalerate— is manifested by the formation of a condensation product of the acetoacetic type, presumably according to the following equation



$$CH_3-CH(CH_3)-CH_2-C(=O)-OC_2H_5 + H-CH(CH(CH_3)-CH_3)-C(=O)-OC_2H_5 \xrightarrow{iso\text{-}C_3H_7MgBr} C_2H_5OH + CH_3-CH(CH_3)-CH_2-C(=O)-CH(CH(CH_3)-CH_3)-C(=O)-OC_2H_5.$$

The structure of the ethyl-α-isovalerylisovalerate formed was demonstrated by the ketone cleavage reaction and subsequent identification of isovalerone among the ketone hydrolysis products.

It is of interest to compare the action of isopropylmagnesium bromide on ethyl isovalerate with its action on isovaleryl acid chloride [2]. In the second case, the yield of reduction products (isopropylisobutylcarbinol and an ester, product of its esterification with isovaleric acid) was considerably greater and reached 40%.

In the second part of the present work, with the object of synthesizing compounds with new structures, the reducing action of secondary alkylmagnesium halides on tertiary acid chlorides was utilized, and led to the formation of significant quantities of secondary alcohols of composition RCHOHR' [3].

Selection of starting materials for the organomagnesium synthesis had to provide for preparation of secondary alcohols of branched structure, the hydrocarbon skeleton of which corresponded to the structure of as yet unsynthesized decanes. Two analogous syntheses were based on the following starting products: the synthesis of 2,4-dimethyl-4-

ethylhexanol-3 from methyldiethylacetyl chloride and isopropylmagnesium bromide and the synthesis of 2,2-dimethyl-4-ethylhexanol-3 from trimethylacetyl chloride and sec.-symm.-amylmagnesium bromide.

As a result of the reaction of methyldiethylacetyl chloride with isopropylmagnesium bromide, the secondary alcohol 2,4-dimethyl-4-ethylhexanol-3 was obtained with a yield of about 26% and the primary β-methyl-β-ethylbutyl alcohol, a product of the reduction of the initial acid chloride, previously investigated by A. E. Favorsky [4], was obtained with a yield of about 25%.

The exptected reaction product – a secondary alcohol of molecular formula $C_{10}H_{21}OH$ – was not obtained as a result of carrying out of the second synthesis, which was probably associated with the considerably greater steric hindrance caused by the symm.-sec.-amyl radical. In the reaction products there was detected neopentyl alcohol in a yield of about 24% – this last a reduction product of the trimethylacetyl chloride, a product of its esterification and a hydrocarbon (3,4-diethylhexane) formed by the coupling of two molecules of the alkyl halide. In this case, elongation of the hydrocarbon skeleton of the original carbonyl-containing compound at the expense of the alkyl halide did not occur.

EXPERIMENTAL

1. Reaction of the Ethyl Ester of Isovaleric Acid with Isopropylmagnesium Bromide

256 g (2.1 mole) of isopropyl bromide with a b.p. of 59-60°, 45 g (1.8 g-atom) of magnesium shavings, and 85 g (0.65 mole) of ethylisovalerate with a b.p. of 135° were used as reactants. The ester was poured into the ethereal solution of alkylmagnesium halide. The reaction was conducted at a temperature at which the ether boiled weakly. The reaction product was fractionally distilled. The approximately 40% of the ester that failed to react was isolated; the remaining portion consisted of the product of an anomalous reaction and intermediate products of the normal reaction from which isopropylisobutyl ketone and isopropylisobutylcarbinol were isolated in approximately equal quantities.

The ketone in the fraction with a b.p. of 144-146° (obtained in a quantity of 8.2 g, d_{20}^{20} 0.8303, n_D^{20} 1.4083) was identified by its semicarbazone which melted at 142°. A sample mixed with isopropylisobutylketone did not give a melting point depression.

Isopropylisobutylcarbinol was identified in the fraction with a b.p. of 154-157° (obtained in a quantity of 7.7 g, d_{20}^{20} 0.8166, n_D^{20} 1.4221) via its phenylurethane which melted at 56-57°. An isolated sample of the fraction was oxidized with a chrome mixture. Isopropylisobutylketone was isolated from the oxidation products and identified in the form of its semicarbazone with a m.p. of 142°.

In addition, a condensation product with a b.p. of 112-113° (10 mm), d_{20}^{20} 0.9284, n_D^{20} 1.4322; MR_D 59.82; calculated 59.28, was obtained in a yield of about 14% of the ester.

3.43 mg sub.: 8.64 mg CO_2; 2.92 mg H_2O. 7.09 mg sub.: 17.82 mg CO_2; 5.91 mg H_2O. Found %: C 68.74, 68.59; H 9.52, 9.35. $C_{12}H_{22}O_3$. Calculated %: C 67.3; H 10.3.

In order to demonstrate its structure the condensation product was subjected to ketone cleavage by three distinct methods: 1) boiling with a 10% aqueous solution of Na_2CO_3 for 2 hours; 2) boiling with a 10% alcoholic solution of potassium hydroxide for 2 hours; and 3) heating in a sealed tube with a 8% aqueous solution of Na_2CO_3 for 8 hours at 225° [5]. Indication of the degree of hydrolysis was furnished by change in n_D^{20}. In the cases of treatment with an alcoholic solution of potassium hydroxide and after heating in the sealed tube there was simultaneous diminishing of the index of refraction from n_D^{20} 1.4322 to n_D^{20} 1.4212-1.4213. Treatment of the condensation product with an aqueous solution of soda without pressure did not cause cleavage.

The product of alkaline hydrolysis had a pleasant fruity odor and on treatment with semicarbazide gave in excellent yield a crystalline derivative with a m.p. 120-121° (according to data in the literature, the semicarbazone of isovalerone has a m.p. of 121° [6]).

3.44 mg sub.: 0.639 ml N_2 (22.5°, 744 mm). 4.08 mg sub.: 0.755 ml N_2 (21.5°, 739 mm). Found %: N 20.96, 20.86. $C_{10}H_{21}ON_3$. Calculated %: N 21.1.

Analysis of the condensation product and the product of its alkaline cleavage thus gives a basis for assuming that our product was ethyl-α-isovalerylisovalerate.

2. Reaction of Methyldiethylacetyl Chloride with Isopropylmagnesium Bromide

(In collaboration with N. D. Snegurovskaya)

The methyldiethylacetyl chloride prepared in a quantity of 50 g had the following constants: b.p. 153-154°, n_D^{20} 1.4368, d_{20}^{20} 0.9955; MR_D 39.78; calculated 39.77.

150 g (1.2 mole) of isopropylbromide, 26.4 g (1.2 g-atom) of magnesium shavings, and 50 g (0.3 mole) of methyldiethylacetyl chloride were used in the reaction. The reagents were added directly and the reaction was conducted at a temperature at which the ether boiled weakly. The reaction product was decomposed by shaking with cracked ice, after which the ester was separated and the residue steam distilled. The free acid was eliminated from the reaction products by treatment with alkali.

Fractions with boiling points of 86-90° (8.7 g) and 109.5-111° (9.1 g) were obtained in very good yield by vacuum distilling the reaction products (at 50 mm). The first fraction had a n_D^{20} of 1.4328. A portion of the fraction was acidified with a chrome mixture and a semicarbazone with a m.p. of 174° was obtained from the acidification products. According to data in the literature [3], the semicarbazone of methyldiethylacetaldehyde has exactly this melting point. The first fraction was consequently a primary alcohol, the reduction product of methyldiethylacetyl chloride.

The fraction with a b.p. of 109.5-111° (50 mm) had the following constants: n_D^{20} 1.4463, d_{20}^{20} 0.8621. Its hydroxyl content was investigated by Verley's method. Found %: OH 10.51. $C_{10}H_{21}OH$. Calculated %: OH 10.70.

A naphthylurethane was obtained from the fraction with a b.p. of 109.5-111° which, after recrystallization from ligroin and ethyl alcohol, melted at 60°.

6.23 mg sub.: 0.265 ml N_2 (24.5°, 748 mm). 5.08 mg sub.: 0.212 ml N_2 (24.5°, 748 mm). Found %: N 4.64, 4.71. $C_{21}H_{29}O_2N$. Calculated %: N 4.3.

An acetyl ester with the following constants: b.p. 205°, n_D^{20} 1.4330, d_{20}^{20} 0.8753; MR_D 59.34; calculated 59.27, was obtained from the alcohol by Spasov's method [7].

Investigation of the fraction with a b.p. of 109.5-111° demonstrated it to be an alcohol with the composition $C_{10}H_{21}OH$.

3. Reaction of Trimethylacetyl Chloride with Symm.-sec.-amylmagnesium Bromide

(In collaboration with N. D. Snegurovskaya)

148 g (1 mole) of 3-bromopentane with a b.p. of 114.5-116°, n_D^{20} 1.4440, prepared frompentanol-3 by Sherill's method [8], 24 g (1 g-atom) of magnesium shavings and 45 g (0.37 mole) of trimethylacetyl chloride with a b.p. of 103° were taken as reactants. Two fractions were isolated from the reaction products with boiling points: 1) 112-114° in a quantity of 7.95 g, n_D^{20} 1.3953; and 2) 91-96° (97 mm) in a quantity of 11.8 g, n_D^{20} 1.3950.

The fraction with a b.p. of 112-114° was investigated for content of tertiary butylcarbinol – a product of the initial reduction in the acid chloride reaction. According to the literature, tertiary butylcarbinol (neopentyl alcohol) has a n_D^{20} 1.3950 and forms a phenylurethane with a m.p. of 114° [3]. By treating a sample from the fraction with a b.p. of 112-114°, a crystalline phenylisocyanate was obtained with a m.p. of 114°, which indicated the presence of neopentyl alcohol in the given fraction.

The fraction with a b.p. of 91-96° (100 mm) was investigated for its content of an ester with a composition $C_4H_9COOC_5H_{11}$ by saponification with an alcoholic solution of alkali; after distilling off the unsaponified portion, an acid was identified in the saponification products. The saponification number of the fraction with a b.p. of 91-96° was 105, which corresponded to a 32.5% ester content.

0.0592 g sub.: 0.0307 g Ag. Found %: Ag 51.85. $C_5H_9O_2Ag$. Calculated %: Ag 51.67.

We assumed that neopentyl alcohol was present in the unsaponified portion, which was carefully washed with water for elimination of the ethyl alcohol. However, attempted preparation from the unsaponified product of a phenylurethane, and of a semicarbazone from the product of its oxidation with chrome mixture, did not give positive results. Evidently the difficulty of demonstrating the presence of the alcoholic ester component – neopentyl alcohol – is to be explained by its great volatility and marked solubility in water.

Further investigation of the unsaponified product showed that it was the hydrocarbon 3,4-diethylhexane, since it had the following constants: b.p. 157-158°, n_D^{20} 1.4188. According to the literature, 3,4-diethylhexane has a b.p. of 158.5-159.5° (764 mm), n_D^{20} 1.4189 [9].

7.02 mg sub.: 20.69 mg CO_2; 9.41 mg H_2O. 4.67 mg sub.: 14.44 mg CO_2; 6.51 mg H_2O. Found %: C 84.22, 84.38; H 15.70, 15.60. $C_{10}H_{22}$. Calculated %: C 84.5; H 15.5.

SUMMARY

1. It was demonstrated that the reaction of ethylisovalerate with a threefold quantity of isopropylmagnesium bromide leads to the formation of a ketone of the RCOR' type, which is partially reduced to the alcohol —isopropylisobutylcarbinol— by the action of alkylmagnesium halides. When subjected to the action of isopropylmagnesium bromide, ethylisovalerate condenses to form a product of the acetoacetic ester type with a yield of 14%.

2. The reducing action of secondary Grignard reagents on tertiary acid chlorides leads to the formation of considerable quantities of an alcohol of the composition RCHOHR, and was utilized for the synthesis of the new alcohol 2,4-dimethyl-4-ethylhexanol-3. The fundamental physico-chemical constants were determined for the latter, and the naphthylurethane and acetyl ester derivatives were characterized.

3. Contrary to indications in the literature on the considerable steric hindrance caused by two ethyl and one methyl groups on the carbon atom in a position α to the carbonyl group [10], methyldiethylacetyl chloride, employed in the synthesis, showed itself capable of forming an alcohol of the composition RCHOHR' with a yield up to 26%.

4. It was shown that symm.-sec.-amylmagnesium bromide gives rise in the organomagnesium synthesis to more considerable steric hindrance than the isopropylmagnesium bromide, inasmuch as, under the very same synthesis conditions it reacts with trimethylacetylchloride to form an alcohol with the composition RCHOHR' in a yield of 53%.

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* See Consultants Bureau Translation, page 1991.

INVESTIGATION IN THE FIELD OF COMPOUNDS CONTAINING A THREE-MEMBERED OXIDE RING

X. THE REACTION OF THE ETHYL β,β-PENTAMETHYLENEGLYCIDATE WITH ANILINE

V. F. Martynov

In one of the preceding communications [1] the investigation of the mutual reaction of aniline with ethyl β,β-tetramethyleneglycidate was described. Addition of aniline also proceeds in this case according to the rule, found by us to be general, of addition of aromatic amines to glycidic acids with a tertiary carbon atom in the β-position.

In approaching the present investigation, we were interested not so much in the question of the locus of rupture of the oxide ring of β,β-pentamethyleneglycidic acid under the action of aniline, inasmuch as this was more or less clear on the basis of our preceding works, as in the question of the ease with which the oxide ring opened and in particular the possibility of conversion to indole homologs.

We obtained ethyl β,β-pentamethyleneglycidate by a method somewhat different from that set forth in the literature, namely by the action of finely divided sodium on a mixture of cyclohexanone with ethyl monochloroacetate. This method was more convenient to carry out and gave yields no less than in the case of condensation with the use of sodium ethylate. It was also established by us in this case that the influence of temperature was not so sharply reflected in the yield of glycidate as was taken for granted in the literature [2]. United States' authors obtained glycidate by employing sodium ethylate at a temperature of −80° and their yield reached 69% [3]. We conducted the reaction in the 0 to + 5° range and obtained glycidate with a yield of 65%.

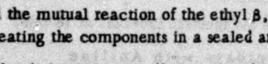
We conducted the mutual reaction of the ethyl β,β-pentamethyleneglycidate with aniline, as in all the remaining cases, by heating the components in a sealed ampoule at 170-180°.

In dealing with ethyl β,β-tetramethyleneglycidate we encountered heightened reactivity of the oxide ring and explained it on the grounds that the planar structure of the five membered ring creates minimumsteric hindrance. In the presence of a six-membered hydroaromatic ring, one may expect increased steric hindrance during the addition of aromatic amines. Actually as shown by experiment, addition of aniline to ethyl β,β-pentamethyleneglycidate proceeds with more difficulty than to ethyl tetramethyleneglycidate.

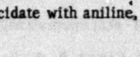
Consequently, and as was demonstrated in this case, the steric hindrance of groups substituted in the β-position strongly influences the addition rate of aromatic amines to glycidic acids with tertiary carbon atoms in the β-position.

On the basis of all the preceding experiments we may ascribe the structure of ethyl α-hydroxy-β-anilino-β,β-pentamethylenepropionate (I) to the addition product of aniline to ethyl β,β-pentamethyleneglycidate.

The correctness of this assumption was verified by the fact that under the influence of concentrated sulfuric acid, the indicated compound split off carbon dioxide, which, as is well known, is a characteristic property of α-hydroxy acids and also, as was shown in our earlier investigations, of α-hydroxy-β-amino acids. We were able to obtain a conclusive demonstration by detecting a second fragment of the molecule. By the very nature of the reaction, 1-anilinohexahydrobenzaldehyde (II) should be the second fragment of the splitting off of carbon dioxide from α-hydroxy-β-amino acids.

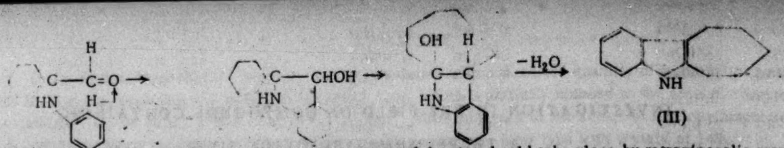


(I)



(II)

Judging by our previous investigations, the indicated aldehyde could not be stable in the given conditions and should be converted into 2,3-pentamethyleneindole (III). This conversion can be depicted in the following manner:



(III)

As is evident from the scheme set forth, enlargement of the ring should take place by retropinacolic rearrangement. We have already observed similar ring enlargement many times, for example in the transformation of α-hydroxy-β-anilino-β,β-tetramethylenepropionic acid as a result of the action of sulfuric acid [1]. Preparation of tetrahydrocarbazole in this case has been exhaustively substantiated and we are fully justified in introducing it in this scheme, the more so, inasmuch as the compound we obtained actually agreed in its constants with the 2,3-pentamethyleneindole synthesized for the first time by Perkin and Plant by Fischer's method, starting from the phenylhydrazone of cycloheptanone [4].

A quantitative yield of 2,3-pentamethyleneindole is obtained in our method, thanks to which this method can be utilized for the synthesis of 2,3-pentamethyleneindole itself as well as of its homologs, especially since the starting products necessary for this synthesis are more available than the cycloheptanone required in the synthesis according to Fischer's method.

EXPERIMENTAL

Synthesis of Ethyl β,β-Pentamethyleneglycidate

A mixture of 49 g of cyclohexanone (0.5 mole) and 61 g (0.5 mole) of the ethyl monochloroacetate was added in drops during energetic stirring to 11.5 g of finely divided sodium in toluene. In the beginning the addition of the mixture was conducted at room temperature, but, as soon as heating was observed, the flask was agitated in a cooling mixture and further addition of the components was conducted at such a rate that the temperature of the reaction mixture did not rise about +5°. Visible separation of sodium chloride did not proceed, in spite of the fact that all the sodium disappeared. After the reaction was completed, the mixture was heated 30 minutes on a water bath; this induced separation of sodium chloride. The reaction mixture was shaken with water, and the toluene layer was separated, dried with sodium sulfate and, after distilling off the toluene, vacuum distilled.

Ethyl β,β-pentamethyleneglycidate distills over in the interval 130-131° at 18 mm. Yield: 60 g (65%).

Reaction of Ethyl β,β-Pentamethyleneglycidate with Aniline

Synthesis of ethyl α-hydroxy-β-anilino-β,β-pentamethylenepropionate. 20 g of ethyl β,β-pentamethyleneglycidate was heated in a mixture with 30 g of aniline in a sealed ampoule for 16 hours at 170-180°. The reaction mixture was slightly colored when the tube was opened at low pressure. By vacuum distilling at 164-167° and 1 mm, a faintly yellow, very viscous liquid distilled over in a quantity of 15 g, which constituted 50% of the theoretical yield. The liquid crystallized on the next day. After recrystallization from ligroin it was obtained in needle-like crystals with a m.p. of 96-97°.

0.1914 g sub.: 8.5 ml N_2 (18°, 774 mm). 0.1449 g sub.: 6.5 ml N_2 (20°, 759.5 mm). Found %: N 5.24, 5.15. $C_{16}H_{23}O_3N$. Calculated %: N 5.05.

Reaction of Ethyl α-Hydroxy-β-anilino-β,β-pentamethylenepropionate with Concentrated Sulfuric Acid

Synthesis of 2,3-pentamethyleneindole. 3 g of ethyl α-hydroxy-β-anilino-β,β-pentamethylenepropionate was mixed with 30 ml of concentrated sulfuric acid. Mutual solution of the substances occurred on heating, with formation of a transparent colorless solution. When the temperature of the reaction mixture rose to 95°, evolution of carbon dioxide bubbles began, which became very intense at 110°. Heating was not continued above 110°. The reaction mass had a golden-yellow color.

After carbon dioxide evolution ceased, the hot reaction mass was poured out on ice, crystals of 2,3-pentamethylindole were filtered off and washed with water; the yield was quantitative. After recrystallization from absolute alcohol, flaky crystals with an oily sheen and a m.p. of 144-145° were obtained. According to the literature, the m.p. is 144° [4]. The nitrogen content agreed with the formula 2,3-pentamethyleneindole. The picrate consisted of needles with a dark brown color and a metallic luster, and had a m.p. of 141-142°. According to the literature, the melting point of the picrate is 142° [4].

SUMMARY

1. The mutual reaction of ethyl β,β-pentamethyleneglycidate with aniline was studied. It was established that the oxide ring of glycidic acid is opened at the β-carbon atom, and forms ethyl α-hydroxy-β-anilino-β,β-pentamethylenepropionate.

2. The conversion from ethyl α-hydroxy-β-anilino-β,β-pentamethylenepropionate to 2,3-pentamethyleneindole was accomplished, and appears to be a new method of synthesizing the latter.

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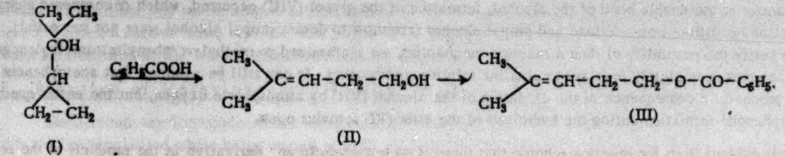
* See Consultants Bureau Translation, page 1739.

THE MECHANISM OF THE TRANSFORMATIONS OF TERTIARY ALCOHOLS OF THE CYCLOPROPANE SERIES UNDER THE INFLUENCE OF MINERAL AND ORGANIC ACIDS

IV. THE REACTION OF DIMETHYLCYCLOPROPYLCARBINOL WITH BENZOIC ACID AND OF METHYLPHENYLCYCLOPROPYLCARBINOL WITH DILUTE FORMIC ACID

T. A. Favorskaya and N. V. Shcherbinskaya

In all the investigations in the field of the transformations of alcohols of the cyclopropane series which we conducted earlier [1-7], we utilized strong acids (HCl, H_2SO_4, HCOOH) as activating agents. The results showed that the acidity of the medium influences both the isomerization of the cyclic alcohols which were investigated into alcohols of the β-ethylenic series, and the cyclization of these latter into tetrahydrofuran derivatives, which induced us to study the reaction of dimethylcyclopropylcarbinol (I) with a weaker acid —benzoic. A primary unsaturated alcohol, 2-methylpenten-2-ol-5 (II), and its corresponding benzoic ester (III) were obtained by reaction of this alcohol with 50% benzoic acid:



The residual fractions consisted of a mixture of the starting cyclic alcohol containing an insignificant quantity of acetyltrimethylene not entering into the reaction, an unsaturated alcohol and its ester. By reaction with benzoic acid considerably more of the starting cyclic alcohol was transformed than in the case of the other acids studied, in spite of a more prolonged heating (4 hours instead of 2-2.5 hours).

It is of interest that dimethyltetrahydrofuran was not detected in the reaction products. The structure of the ester obtained was demonstrated both by hydrolysis and by decomposing it with $MgBrC_6H_5$, the result in both cases being the formation of the primary alcohol (II), the constants of which agreed well with the known literature data. Triphenylcarbinol was obtained along with the primary alcohol by the action of $MgBrC_6H_5$.

In order to elucidate the reaction mechanism it was desirable to isolate as large a number of intermediate products as possible. Various acids at differing concentrations were used to this end. However, the influence of acid concentration proper on the isomeric transformations of alcohols could not thus be clarified.

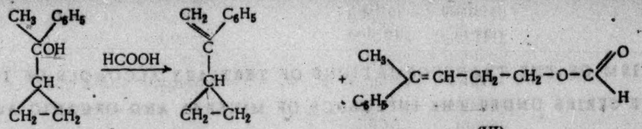
In order to clarify this question, we measured the pH of the acids employed. Reagent acidity most noticeably influences the cyclization of primary alcohols which are derivatives of tetrahydrofuran The dependence of yield of cyclic products on pH can be presented in tabular form.

TABLE

Alcohol	pH of reagent					
	−0.37 HCOOH 80%	0.19 H_2SO_4 1:5	0.33 H_2SO_4 1:10	0.44 HCOOH 1:1	0.88 HCOOH 1:2	1.7-2.0 C_6H_5COOH 50%
Dimethylcyclopropylcarbinol	–	–	51.6%	19.2%	–	0%
Methylethylcyclopropylcarbinol	52.6%	24%	–	–	9.6%	–

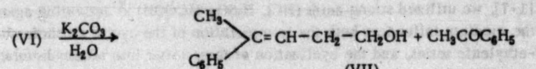
Although this table is far from complete, it is nevertheless evident from it that the greater the acidity of the medium, the greater is the yield of tetrahydrofuran derivatives.

In a reaction already studied by us [4], the reaction of methylphenylcyclopropylcarbinol (IV) with concentrated formic acid, there was obtained a significant quantity of the hydrocarbon —phenylcyclopropylethylene (V) and a small quantity of the formyl ester of the primary unsaturated alcohol (VI)



(IV) (V) (VI)

By taking a greater quantity of the alcohol (IV) and a more dilute acid, we were able to obtain, in addition to the hydrocarbon (V) and the ester (VI), a certain quantity of the unsaturated primary alcohol 2-phenylpenten -2-ol-5 which could not be isolated from its formyl ester by redistillation, in view of the proximity of their boiling points. The mixture of these two substances was subjected to hydrolysis, as a result of which there was obtained 2-phenylpenten -2-ol-5 and acetophenone in a yield of 1.7%.

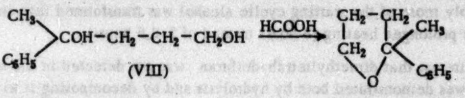


$$(VI) \xrightarrow[H_2O]{K_2CO_3} (CH_3)(C_6H_5)C{=}CH-CH_2-CH_2OH + CH_3COC_6H_5$$

(VII)

The formation of acetophenone was unexpected, but not accidental, inasmuch as it was redetected when the experiment was repeated. To explain its formation it could be assumed that, as a result of the addition of a molecule of water at the double bond of the alcohol, formation of the glycol (VIII) occurred, which decomposed under the reaction conditions into a ketone and propyl alcohol (attempts to detect propyl alcohol were not successful). In order to verify the possibility of such a reaction mechanism, we synthesized α-methyl-α-phenyltetramethyleneglycol; it was, however, completely resistant to alkaline solution and heating. It can still be assumed that acetophenone formation proceeds in consequence of the oxidation of the alcohol (VII) by atmospheric oxygen, but the entire question of acetophenone formation during the hydrolysis of the ester (VI) remains open.

It is evident from the reaction scheme that there is no tetrahydrofuran derivative in the products of the action of HCOOH on the alcohol (IV); the primary alcohol (VII) does not isomerize under these conditions. 2,2-Methylphenyltetrahydrofuran was obtained only by the action of formic acid on the glycol (VIII)



(VIII) (IX)

The fact that the alcohol does not give a tetrahydrofuran derivative may possibly result from the lower acid concentration used (1:1) (tetrahydrofuran was obtained by the action on the glycol of 80% HCOOH), or the difficulty of oxide formation from phenylpenten -2-ol-5 may be explained by the presence in the alcohol molecule of a conjugated double bond system. Formation of a cyclic compound calls for disturbance of a stable system, which is energetically improbable.

The results of the present work and those presented in the three preceding communications show that the reaction of tertiary alcohols of the cyclopropane series with organic acids and with sulfuric acid proceeds by the same mechanism: in the first stage of the reaction the cyclic alcohol is isomerized into a primary alcohol of the ethylenic series which then undergoes various transformations depending on the activating acid. The pH of the reagent influences both the first stage and the further transformations.

EXPERIMENTAL

1. Reaction of Dimethylcyclopropylcarbinol with Benzoic Acid

70 g of dimethylcyclopropylcarbinol prepared and purified in the usual way [5], was added to a hot solution of 170 g of benzoic acid in 170 ml of water. The mixture was boiled with a reflux condenser for 4 hours. The hot solution was then neutralized with NaOH solution to neutral reaction. The reaction products were extracted with ether. After drying and distilling off the solvent, the residue was initially distilled at ordinary pressure and then the high boiling point fractions were separated by vacuum distillation. The following fractions were obtained: 1st 116-125°, 7.9 g (11.3%), n_D^{16} 1.4320; 2nd 125-140°, 13.45 g (19.2%); 3rd 140-152°, 2.5 g (3.6%); 4th 152-157°, 4.1 g (5.8%), n_D^{16} 1.4468; 5th at 142° (10 mm), 3.4 g; 6th 142-144° (10 mm), 17.5 g (12%).

The first fraction consisted of the starting alcohol, the two following – a mixture of a cyclic and unsaturated alcohol, the fourth – the primary alcohol 2-methylpenten -2-ol-5, the last – the benzoyl ester of this alcohol.

Investigation of the Substance with a b.p. of 142-144° (10 mm) (6th fraction): The substance boils at 272-274° (760 mm); d_4^{20} 1.0103; d_4^{0} 1.0252; n_D^{20} 1.5125; MR_D 60.62. $C_{13}H_{16}O_2\overline{F}_3$. Calculated: MR_D 59.82.

0.0752 g sub.: 0.2115 g CO_2; 0.0544 g H_2O. Found %: C 76.70; H 8.09. $C_{13}H_{16}O_2$. Calculated %: C 76.47; H 7.84.

a) Action of $MgBrC_6H_5$ on the benzoyl ester of 2-methylpenten -2-ol-5. In the preparation of $MgBrC_6H_5$, magnesium was taken in excess in order that there would be no unreacted bromobenzene remaining in the reaction products (2.5 g of Mg and 13.2 g of C_6H_5Br). 8.4 g of the benzoyl ester in absolute ether was added to the organomagnesium compound. The organomagnesium complex was decomposed with water. After drying, distilling off the solvent and redistilling, a fraction was obtained with a b.p. of 152-156°, d_4^{20} 0.8570, n_D^{20} 1.4460, which agreed in its constants with 2-methylpenten -2-ol-5. The residue crystallized in the distillation flask. The melting point of the crystals was 161° (from aqueous alcohol), which agreed with that of triphenylcarbinol.

b) Hydrolysis of the ester. Inasmuch as the ester was very slightly soluble in water, its hydrolysis with a 10% potash solution yielded no result and was rather conducted in a water-alcohol solution of alkali. 10 g of the ester was dissolved in 50 ml of ethyl alcohol to which was added a solution of 11 g of a 50% KOH solution. The reaction was conducted by stirring and heating for 1.5 hours. The reaction products were extracted with ether. After drying, distilling off the ether and redistilling, fractions boiling at 75-152° and 152-155° (53%) were isolated. The latter was redistilled a second time, b.p. 151-155°, n_D^{20} 1.4470, which agreed with the constants of 2-methylpenten -2-ol-5. Upon acidification of the water-alcohol solution, a precipitate of benzoic acid, m.p. 121°, separated out.

2. Reaction of Methylphenylcyclopropylcarbinol with Formic Acid

Methylphenylcyclopropylcarbinol was prepared by the method worked out by Sh. A. Fridman [3]. 60 g of this alcohol was boiled while being stirred with 60 ml of HCOOH (1:1) for 1.5 hours. The formic acid was neutralized with dry soda, the reaction product was extracted with ether. After drying and distilling off the ether, the residue was vacuum distilled. The following fractions were obtained: 1st 88-90° (8 mm), 10.0 g (18.7%); 2nd 138-140° (8 mm), 45.0 g (63%).

The fraction with a boiling point of 88-90° (8 mm): d_4^{21} 0.9618; n_D^{21} 1.5421. MR_D 47.13. $C_{11}H_{12}\overline{F}_4$. Calculated: MR_D 47.07. The constants of this fraction agreed with those of phenylcyclopropylethylene, previously obtained by us.

The fraction with a b.p. of 138-140° (8 mm): d_4^{22} 1.040; d_4^{0} 1.058; n_D^{22} 1.5366. MR_D 56.84. $C_{12}H_{14}O_2\overline{F}_4$. Calculated: MR_D 54.81.

Numerous analyses for C and H gave results intermediate between those calculated for the alcohol and for its ester. The 138-140° fraction (8 mm) reacted energetically with metallic sodium.

Hydrolysis of the substance with a b.p. of 138-140° (8 mm). 20 g of the substance was boiled while being stirred with a 20% solution of K_2CO_3 for 3 days. The products of hydrolysis were extracted with ether. After drying and distilling off the solvent the residue was vacuum distilled. The following fractions were obtained: 1st 120-138° (8 mm), 3 g; 2nd 138-139° (8 mm), 11.1 g (65.3%). The fraction with a b.p. of 120-138° (8 mm) had a strongly pronounced odor of acetophenone and gave a precipitate with 2,4-dinitrophenylhydrazine. With the object of verifying the formation of acetophenone, a second attempt at hydrolysis under the very same conditions was conducted. From 16.4 g of substance about 3 g of acetophenone-containing fractions and 8.1 g (58%) of a fraction with a b.p. of 138-139° (1 mm) were obtained. After distilling the low-boiling fractions for a second time, 1.6 g (~6%) of pure acetophenone and 1.5 g of a mixture of acetophenone and alcohol were isolated from the two experiments. The semicarbazone prepared from the acetophenone gave no melting point depression with the semicarbazone of known acetophenone.

The fraction with a b.p. of 138-139° (8 mm): d_4^{23} 1.032; n_D^{23} 1.5573. MR_D 50.65. $C_{11}H_{14}\overline{F}_4$. Calculated: MR_D 50.09. The constants agreed with those earlier obtained by us for 2-phenylpenten -2-ol-5 [4].

3. Reaction of α-Methyl-α-phenyltetramethyleneglycol with Formic Acid

17 g of acetopropyl alcohol and 50 ml of ether were added to phenylmagnesium bromide prepared from 8 g of Mg and 52 g of bromobenzene, after which the reaction mass was heated for 4 hours and then decomposed with water. The ethereal layer was poured off, while the precipitate of basic Mg salts was washed with ether. After drying and distilling off the ether the residue was vacuum distilled. About 4 g of the acetopropyl alcohol was recovered

unchanged from the reaction; the next fraction crystallized in the condenser and receiving flask, m.p. 67-68° which agreed with that of diphenyl; the last fraction with a b.p. of 200-205° (37 mm) – 16 g (~70% of the acetopropyl alcohol used up in the reaction) – consisted of α-methyl-α-phenyltetramethyleneglycol. It was a very thick, viscous, transparent liquid which did not crystallize on prolonged standing.

0.1176 g sub.: 0.3225 g CO_2; 0.0820 g H_2O. Found %: C 74.78; H 7.80. $C_{11}H_{16}O_2$. Calculated %: C 73.33; H 8.88.

The analytical data indicated that the glycol was evidently contaminated with diphenyl. Attempts to purify it more completely were not successful, due to its viscosity.

7.8 g of the glycol was boiled while being stirred for 2 hours with 80% HCOOH. The formic acid was neutralized with dry soda upon completion of the heating. The reaction products were extracted with ether and dried with Na_2SO_4. The ether was distilled off and the residue vacuum distilled. About 4 g (~57%) of a fraction with a b.p. of 102-107° (14 mm) was obtained.

After it was distilled for a second time, the substance boiled at 102-103° (14 mm): d_4^{20} 1.0073; n_D^{20} 1.5161; MR_D 48.56. $C_{11}H_{14}O\digamma_3$. Calculated: MR_D 48.79.

The data of R. Paul [8] for α-methyl-α-phenyltetrahydrofuran were: b.p. 105-106° (20 mm); d_4^{25} 1.0114; n_D^{25} 1.5179.

Oxidation of α-methyl-α-phenyltetrahydrofuran. 1.2 g of the substance with a b.p. of 102-103° (14 mm) was taken for the oxidation. Decolorization of $KMnO_4$ solution proceeded very slowly and continued for 2 days. 1.6 g of $KMnO_4$ was used up in the oxidation. The manganese dioxide was filtered off and washed with hot water. The filtrate was evaporated to small volume and acidified with sulfuric acid. The oxidation products were extracted with ether. After drying and eliminating the ether with a vacuum, there remained a white crystalline residue with a m.p. of 94-95°. The crystalline lactone obtained dissolved in excess ammonia on being heated. The excess ammonia was driven off. Into the resulting ammonium salt solution was poured a concentrated solution of $AgNO_3$, and the silver salt precipitate was filtered off, washed with water and dried in a vacuum desiccator.

0.0443 g sub.: 0.0159 g Ag. Found %: Ag 35.89. $C_{11}H_{13}O_3Ag$. Calculated %: Ag 35.88.

The analysis agreed with that of the salt of γ-phenyl-γ-hydroxyvaleric acid.

Heating of α-methyl-α-phenyltetramethyleneglycol with 20% potash solution. The experiment was conducted with the object of exploring the possibility of acetophenone formation as a result of the alkaline hydrolysis of the formic ester. 7 g of glycol was heated and stirred for 2 days with a 20% solution of potash. The glycol was recovered unchanged. No acetophenone was detected.

SUMMARY

1. It was established that in the reaction of dimethylcyclopropylcarbinol with 50% benzoic acid, only an unsaturated primary alcohol and its ester are formed.

2. It was demonstrated that in the reaction of methylphenylcyclopropylcarbinol with dilute formic acid, the hydrocarbon, phenylcyclopropylethylene, and a mixture of an unsaturated primary alcohol and its formyl ester, with boiling points close together, are formed.

3. α-Methyl-α-phenyltetramethyleneglycol was synthesized and it was shown that 2,2-methylphenyltetrahydrofuran is formed by heating it with formic acid.

4. It was established that the reaction of tertiary alcohols of the cyclopropane series with organic acids and with sulfuric acid proceeds by the same mechanism.

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* See Consultants Bureau Translation, page 613.

** See Consultants Bureau Translation, page 891.

*** See Consultants Bureau Translation, page 1553.

**** See Consultants Bureau Translation, page 1751.

***** See Consultants Bureau Translation, page 1985.

THE MECHANISM OF THE TRANSFORMATIONS OF TERTIARY ALCOHOLS OF THE CYCLOPROPANE SERIES UNDER THE INFLUENCE OF MINERAL AND ORGANIC ACIDS

V. THE REACTION OF METHYL-n-BUTYLCYCLOPROPYLCARBINOL WITH HYDROCHLORIC ACID, THE REACTION OF DIMETHYLCYCLOPROPYLCARBINOL, METHYLISOPROPYLCYCLOPROPYLCARBINOL AND OF METHYL-n-BUTYLCYCLOPROPYLCARBINOL WITH PHOSPHORUS TRICHLORIDE IN THE PRESENCE OF PYRIDINE

T. A. Favorskaya, T. N. Gulyaeva and E. S. Golovacheva

Investigations conducted by one of us in the field of tertiary alcohols of the cyclopropane series [1, 2, 3], established that a peculiar allyl rearrangement involving migration of a halogen atom to the β-position and opening of the three-membered ring takes place in halides of this series. Upon heating the resulting halides with an aqueous solution of potash, they are reconverted into the initial cyclic alcohols.

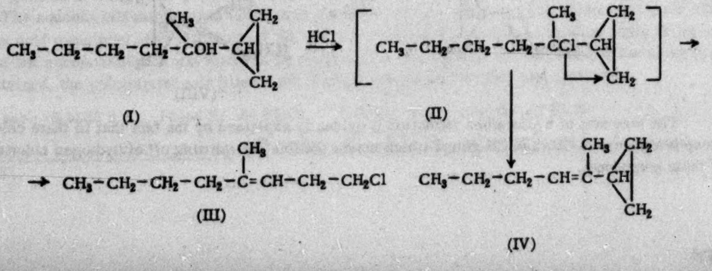
To explain these conversions the following mechanism was proposed. A tertiary cyclic chloride is formed in the reaction of a cyclic tertiary alcohol with hydrochloric acid, which then undergoes the rearrangement indicated above. On hydrolysis of the unsaturated primary chloride that is being formed, migration of the chlorine atom to the γ-position proceeds with formation of a tertiary cyclic chloride which is subsequently hydrolyzed and yields the initial cyclic alcohol.

However, neither during the action of hydrochloric acid on alcohols nor during the hydrolysis of the unsaturated chlorides, were tertiary cyclic chlorides detected.

The first of the rearrangements indicated above was studied by us for methylacetylenylcyclopropylcarbinol and dimethyl- and methylethylcyclopropylcarbinol. The second rearrangement was studied for the two latter alcohols during the hydrolysis of the chloride obtained from methylacetylenylcyclopropylcarbinol; we did not succeed in obtaining the original cyclic alcohol in view of the readiness with which it is polymerized in alkaline media.

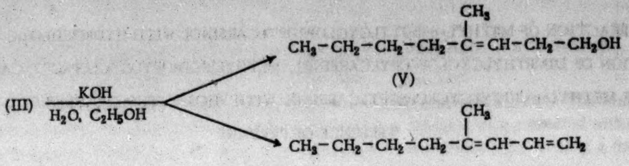
The present work was undertaken on the one hand, in order to extend the above indicated reaction to a more complex homologous tertiary alcohol of the cyclopropane series, methyl-n-butylcyclopropylcarbinol, and on the other hand, in order to obtain the intermediate reaction products — tertiary cyclic chlorides, to demonstrate that they isomerize into unsaturated primary chlorides with open chain carbon atoms and to confirm by this our postulated reaction mechanism.

Methylbutylcyclopropylcarbinol was prepared by the action of butylmagnesium bromide on acetyltrimethylene. The action on it of dilute hydrochloric acid (1:1) at room temperature led to the primary unsaturated chloride — 4-methyl-1-chlorooctene-3, the structure of which was proved by ozonization, which process yielded β-chloropropionic acid and methylbutylketone. In addition to this, thanks to the presence of the CH_2 group adjacent to the tertiary alcoholic group of the cyclic alcohol, the formation of the hydrocarbon 2-cyclopropylhexene-2 proceeded with resultant splitting off of hydrogen chloride from the original primary cyclic chloride being formed. By oxidation of the hydrocarbon with $KMnO_4$ solution, acetyltrimethylene and butyric acid were isolated. These results indicated that by the action of hydrochloric acid on methyl-n-butylcyclopropylcarbinol, exactly the same rearrangement proceeds as for all the other alcohols investigated.



CH₃–CH₂–CH₂–CH₂–COH(CH₃)–CH(CH₂)₂
(I)
HCl
CH₃–CH₂–CH₂–CH₂–CCl(CH₃)–CH(CH₂)₂
(II)
CH₃–CH₂–CH₂–CH₂–C(CH₃)=CH–CH₂–CH₂Cl
(III)
CH₃–CH₂–CH₂–CH=C(CH₃)–CH(CH₂)₂
(IV)

The chloride obtained was subjected to hydrolysis with a boiling 10% solution of potash for 24 hours; however, only unchanged chloride (III) was isolated. The hydrolysis was successfully accomplished only by heating the chloride with a 25% water alcohol solution of KOH. From the reaction products an unsaturated primary alcohol was isolated – 4-methylocten -3-ol-1 (V)– the normal hydrolysis product of the chloride, and the product of elimination of hydrogen chloride from the chloride (III) – the 1,3-diene hydrocarbon (VI)– 4-methyloctadiene-1,3.



$$\text{(III)} \xrightarrow[H_2O,\ C_2H_5OH]{KOH} \begin{cases} CH_3-CH_2-CH_2-CH_2-\overset{CH_3}{\overset{|}{C}}=CH-CH_2-CH_2OH & \text{(V)} \\ CH_3-CH_2-CH_2-CH_2-\overset{CH_3}{\overset{|}{C}}=CH-CH=CH_2 & \text{(VI)} \end{cases}$$

(VI)

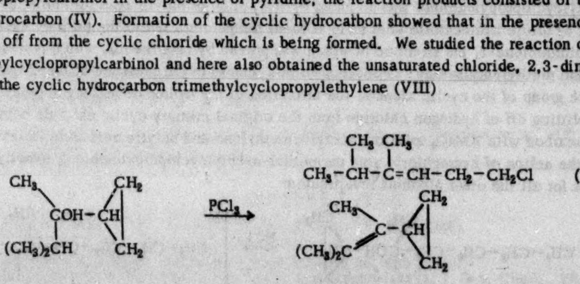
Methylbutylketone and acrylic acid were obtained by ozonization of the alcohol (V). The hydrocarbon (VI) polymerized into a rubber-like polymer on heating in a water bath with maleic anhydride.

Thus, formation of the cyclic alcohol did not occur during hydrolysis of the chloride (III). The very difficulty in the hydrolysis of the chloride (III) itself showed that its isomerization into the chloride (II) did not occur, since in the similar case of the hydrolysis of the tertiary chloride it proceeded readily, and this was also observed for chlorides obtained from the dimethyl- and methylethylcyclopropylcarbinols.

Using methylacetylenylcyclopropylcarbinol as a model, we studied the formation of the chlorides from the tertiary alcohols of the cyclopropane series under various conditions – in the presence of concentrated and dilute (1:1) hydrochloric acid at room temperature, at 0° and at –20°, and also in the presence of phosphorus trichloride; an unsaturated primary chloride was obtained in all cases. Formation of a cyclic chloride – postulated by us as an intermediate reaction product– was not once detected.

Ya. M. Slobodin and I. N. Shokhor [4] employed the method of Bouis [5] in which phosphorus tribromide in the presence of pyridine acted on vinylalkylcarbinol, to prepare the cyclic bromide and chloride corresponding to the secondary alcohol methylcyclopropylcarbinol, desiring thus to avoid addition to the double bond of the hydrogen bromide which is always isolated to a greater or lesser extent in the reaction of alcohols with PBr_3.

Actually, during the action of PCl_3 on methylacetyleneylcyclopropylcarbinol, in addition to the single primary monochloride, we obtained a 1,3-diene dichloride formed by the addition of HCl at the triple bond [1]. By conducting the reaction in the presence of pyridine, Slobodin and Shokhor obtained as a result of the action of PBr_3 on methylcyclopropylcarbinol a mixture of cyclic and unsaturated bromides, and by the action on this alcohol of PCl_3 obtained a cyclic chloride with a small admixture of unsaturated chloride. A tertiary cyclic bromide was obtained by Lipp [6] by the action of PBr_3 on diphenylcyclopropylcarbinol. The stability of this bromide may be explained by the presence in it of two phenyl radicals. We were not successful in obtaining a cyclic chloride by the action of PCl_3 on methylbutylcyclopropylcarbinol in the presence of pyridine; the reaction products consisted of the unsaturated chloride (III) and the hydrocarbon (IV). Formation of the cyclic hydrocarbon showed that in the presence of pyridine hydrogen chloride is split off from the cyclic chloride which is being formed. We studied the reaction of PCl_3 and pyridine with methyl-isopropylcyclopropylcarbinol and here also obtained the unsaturated chloride, 2,3-dimethyl-6-chlorohexene-3 (VII) and the cyclic hydrocarbon trimethylcyclopropylethylene (VIII)

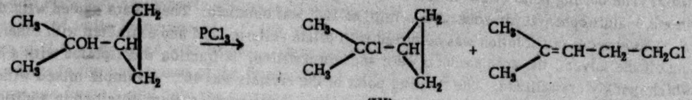


$$CH_3-\overset{CH_3}{\overset{|}{C}H}-\overset{CH_3}{\overset{|}{C}}=CH-CH_2-CH_2Cl \quad \text{(VII)}$$

(VIII)

The readiness of hydrocarbon formation is evidently explained by the fact that in these chlorides the CCl group is adjacent to CH_2 and CH groups which makes possible the splitting off of hydrogen chloride from a molecule of these compounds.

In order to avoid, insofar as possible, the formation of hydrocarbons, we resolved to let PCl_3 act on dimethylcyclopropylcarbinol in the presence of pyridine. In this case we succeeded in selecting suitable conditions and obtained two chlorides: one, the usual unsaturated chloride, the other with a b.p. 30° lower, completely resistant to $KMnO_4$ solution, and with a Raman spectrum in which was detected the intensive frequencies 1190 and 870 cm^{-1}, characteristic of the trimethylene ring.



(IX) (X)

The simultaneous formation of both chlorides indicates that under the conditions of the reaction the cyclic chloride is still partially polymerized into the unsaturated chloride. The faintest traces of moisture can bring about this isomerization during which the lower boiling fraction on repeated redistillation is converted into the higher-boiling unsaturated chloride. No hydrocarbon was detected in the reaction products.

The results obtained thus confirm the correctness of the general mechanism postulated for the formation of unsaturated primary chlorides from tertiary alcohols containing the cyclopropyl radical, by way of intermediate formation of a tertiary cyclic chloride.

EXPERIMENTAL

T. N. Gulyaeva

Methyl-n-butyl-cyclopropylcarbinol was prepared from butylmagnesium bromide and acetyltrimethylene. In contrast to methylisobutylcyclopropylcarbinol and methyltertiarybutylcyclopropylcarbinol, the yield of which was small, this alcohol under these conditions was obtained in a yield of 84%.

B.p. 62-63° (6 mm); d_4^{20} 0.8762; n_D^{20} 1.4463; MR_D 43.28. $C_9H_{18}O$. Calculated 43.74.

Literature data [7]: d_4^{20} 0.8745; n_D^{20} 1.4451.

0.0883 g sub.: 0.2457 g CO_2; 0.1010 g H_2O. 0.1080 g sub.: 17.1 ml CH_4 (18°, 775 mm). Found %: C 75.93; H 12.80; number of active hydrogens 0.99. $C_9H_{18}O$. Calculated %: C 76.05; H 12.67; number of active hydrogens 1.

1. Reaction of Methylbutylcyclopropylcarbinol with Dilute (1:1) Hydrochloric Acid

33 g of methylbutylcyclopropylcarbinol was stirred for 2 hours at room temperature with 65 ml of acid after which the reaction products were separated from the aqueous layer, washed with water, dried with $CaCl_2$ and vacuum distilled. Two fractions were isolated: 1st with a b.p. of 52-53° (15 mm), 9 g (31%) and 2nd with a b.p. of 82-83° (15 mm), 16 g (43%).

The fraction with a b.p. of 52-53° (15 mm): d_4^{20} 0.7929; n_D^{20} 1.4500; MR_D 42.06. $C_9H_{16}\Gamma$. Calculated: MR_D 41.75.

0.0995 g sub.: 0.2849 g CO_2; 0.1163 g H_2O. 0.1183 g sub.: 15.87 g benzene: Δt 0.31°. Found %: C 87.00; H 13.06; M 123.6. C_9H_{16}. Calculated %: C 87.10; H12.90; M 124.

Oxidation. 2.8 g of hydrocarbon was oxidized with $KMnO_4$ solution. 5.6 g of salt went into the oxidation. The MnO_2 was filtered off and extracted with ether while being heated. Neutral products were distilled off from the aqueous solution; the first drops of the distillate gave an abundant precipitate with a 2,4-dinitrophenylhydrazine solution. The m.p. was 144-145° (from alcohol). The very same product was also obtained from the ethereal extract. The precipitate gave no melting point depression with the 2,4-dinitrophenylhydrazone obtained from a known acetyltrimethylene. The aqueous salt solution was concentrated on a water bath, acidified with dilute H_2SO_4 and extracted with ether. The acid remaining after distilling off the ether was treated with ammonia solution while being heated on a water bath; the excess ammonia was removed by evaporation. $AgNO_3$ solution was added to the ammonium salt solution obtained, the precipitated salt filtered off, washed with water, alcohol, and analyzed.

0.0958 g sub.: 0.0530 g Ag. Found %: Ag 55.28. $C_4H_7O_2Ag$. Calculated %: Ag 55.38.

Fraction with a b.p. of 82-83° (15 mm): d_4^{20} 0.8993; n_D^{20} 1.4550; MR_D 48.41. $C_9H_{17}Cl\Gamma$. Calculated: MR_D 48.81.

0.0944 g sub.: 0.0843 g AgCl. Found %: Cl 22.09. $C_9H_{17}Cl$. Calculated %: Cl 22.12.

Ozonization of the chloride $C_9H_{17}Cl$. For the ozonization, 3.6 g of the chloride was taken and dissolved in 40 ml of chloroform. The ozonide obtained after elimination of the solvent was decomposed with water while being heated on a water bath. The aqueous solution obtained was neutralized with soda and the neutral products were steam distilled. The boiling point of the isolated neutral product was determined by Sivolobov's method to be equal to 127°, and a 2,4-dinitrophenylhydrazone with a m.p. of 106° was obtained. These data agreed with those of methylbutylketone. The aqueous salt solution was acidified with dilute sulfuric acid and extracted with ether. After drying and distilling off the solvent, the acid products were vacuum distilled. A fraction was isolated with a b.p. of 90-93° (11 mm), which quickly crystallized. The melting point of the crystals was 40°. A sample mixed with known β-chloropropionic acid gave no melting point depression. No other ozonolysis products were obtained in addition to methylbutylketone and β-chloropropionic acid.

Hydrolysis of 4-methyl-1-chlorooctene-3. 16 g of the chloride, 20 ml of 50% aqueous solution of KOH and 20 ml of alcohol were boiled while being stirred for 24 hours, after which the upper layer ceased to give the Beilstein halogen reaction. The upper layer was separated and the aqueous layer was extracted with ether; after drying and distilling off the ether the products of hydrolysis were vacuum distilled. The fractions obtained were: 1st b.p. 60-62° (25 mm), 0.88 g; 2nd b.p. 91-95° (15 mm), 4.6 g. A large quantity of resin remained in the distillation flask.

Fraction with a b.p. of 60-62° (25 mm): d_4^{20} 0.7699; n_D^{20} 1.4605; MR_D 44.11. $C_9H_{16}\digamma_2$. Calculated, 42.83. The substance quickly decolorized $KMnO_4$ solution and did not give a hydroxide reaction. In order to demonstrate the presence of conjugated double bonds which was suggested by the heightened molecular refraction, an attempt was made to condense the hydrocarbon with maleic anhydride. 0.88 g of hydrocarbon was heated with 0.69 g of maleic anhydride. On cooling a homogeneous, transparent, rubber-like product formed. The data obtained permit us to assume that the hydrocarbon formed consisted of 4-methyloctadiene-1,3.

Fraction with a b.p. of 91-95° (15 mm): d_4^{20} 0.8199; n_D^{20} 1.4400; MR_D 45.66; $C_9H_{18}O\digamma$. Calculated, 44.82.

0.1135 g sub.: 19.5 ml CH_3 (14°, 762 mm). OH number 0.98. $C_9H_{18}O$. Calculated OH number 1.

In view of the small quantity of substance present, we did not succeed in purifying it sufficiently from hydrocarbon admixture, and determination of the percentage hydrocarbon composition gave an exaggerated result.

0.0909 g sub.: 0.2591 g CO_2; 0.1001 g H_2O. Found %: C 77.78; H 12.32. $C_9H_{18}O$. Calculated %: C 76.05; H 12.67.

Ozonization of the alcohol with a b.p. of 91-95° (15 mm). 3.9 g of the substance was ozonized in chloroform. After eliminating the solvent the ozonide obtained was decomposed with water while being heated on a water bath. After neutralizing the solution with soda the neutral products were steam distilled. The product isolated gave a 2,4-dinitrophenylhydrazone with a m.p. of 106° which coincided with that of methylbutylketone. The aqueous solution of salts was acidified with dilute sulfuric acid and extracted with ether. After drying and distilling off the solvent, the acid liquid remaining was heated on a water bath with ammonia until it dissolved. Excess ammonia was evaporated off. $AgNO_3$ solution was added to the ammonium salt solution obtained. The salt precipitate was analyzed.

0.1101 g sub.: 0.0662 g Ag. Found %: Ag 60.14. $C_3H_3O_2Ag$. Calculated %: Ag 60.33.

2. Reaction of Methylbutylcyclopropylcarbinol with Phosphorus Trichloride in the Presence of Pyridine

In view of the ease with which tertiary chlorides hydrolyzed with resultant formation of hydrochloric acid and consequent isomerization of the tertiary cyclic chloride into an unsaturated chloride with an open chain of carbon atoms, we turned to the method employed by Slobodin and Shokhor [4]. These authors treated the reaction products with ice water to dissolve H_3PO_3 and extracted the chlorides and bromides subsequently obtained with ether. To avoid the faintest traces of moisture, which can cause the hydrolysis of the chloride, we blended the active liquid reaction products with a thick mass of H_3PO_3, but, in spite of these precautions, we did not succeed in obtaining methylbutylcyclopropylchloromethane.

37.7 g of methylbutylcyclopropylcarbinol and 7.5 g of pyridine were poured in drops into 12.2 g of PCl_3, stirred in a cylinder with a stirrer and cooled with ice water. Upon completion of the addition, the reaction products were left to stand for 2 hours, after which the liquid was blended with H_3PO_3 and dried with Na_2SO_4 overnight. By vacuum distillation, two fractions were obtained, agreeing in properties with 4-methyl-1-chlorooctene-3 with a n_D^{20} of 1.4555 and 2-cyclopropylhexene-2 with a n_D^{20} 1.4490.

The experiment was repeated several times and each time with several of the conditions varied, but only the products described above were obtained as a result.

3. Reaction of Dimethylcyclopropylcarbinol with Phosphorus Trichloride in the Presence of Pyridine.

24.3 g of dimethylcyclopropylcarbinol and 5.4 g of pyridine were added in drops to 11.3 g of PCl_3. The reaction was conducted while being cooled with ice water. Upon completion of the addition, the liquid was blended with a solid mass of H_3PO_3 and dried with Na_2SO_4. The experiment was repeated 5 times. In these cases, while the distillation products in the upper parts of the fractionation column consisted of droplets of water, the lower-boiling fractions were not formed, and only the unsaturated chloride was obtained. Several drops of pyridine were added in addition to the product obtained after blending with H_3PO_3 in the last experiment. On the following day when the substance was distilled there were obtained two fractions: 1st with a b.p. of 104-105°, 3.6 g (12.2%) and 2nd with a b.p. of 130-132°, 8.3 g. An intermediate fraction obtained in a quantity of 6.7 g with a b.p. of 105-130° could not be fractionally distilled because it all distilled with the following fraction at 130-132°.

Fraction with a b.p. of 104-105°: d_4^{20} 0.9380; n_D^{20} 1.4395; MR_D 33.21. $C_6H_{11}Cl$. Calculated 33.23.

The substance obtained did not react with $KMnO_4$ and contained no admixture of hydrocarbon; determination of the percentage composition of chlorine gave very good results.

0.1108 g substance: 0.1360 g AgCl. 0.1027 g substance: 13.57 g benzene: Δt 0.315°. Found %: Cl 30.14; M 123.2. $C_6H_{11}Cl$. Calculated %: Cl 29.95; M 118.5.

To confirm the cyclic nature of the chloride, the Raman spectrum was determined:

339(3), 367(2), 499(3), 515(2), 541(1), 580(1), 648(3), 714(1), 735(3), 756(5), 768(2), 774(1), 823(5), 858(3), 870(6), 983(1), 1016(1), 1030(2), 1098(1), 1121(1), 1190(8), 1668(1), 1686(1), 1693(2), 1702(3), 1711(1) (frequencies in cm^{-1}).

The second fraction agreed in its properties with the unsaturated chloride 2-methyl-5-chloropentene-2.

E. S. Golovacheva

4. Reaction of Methylisopropylcyclopropylcarbinol with Phosphorus Trichloride in the Presence of Pyridine.

A mixture of 10 g of methylisopropylcyclopropylcarbinol and 1.9 g of pyridine was added to 3.5 g of PCl_3. The reaction was conducted while the reactants were cooled with ice water. Upon completion of the reaction the upper layer was carefully blended with H_3PO_3 and dried with Na_2SO_4. It was fractionally distilled into the two fractions: 1st 133-158°, 0.7 g, 2nd 168°, 3.5 g.

Fraction with a b.p. of 133-158°: d_4^{20} 0.8426; n_D^{20} 1.4520; MR_D 46.93. $C_8H_{15}Cl$ F. Calculated 43.54.

0.1068 g substance: 0.1662 g AgCl. Found %: Cl 15.30. $C_8H_{15}Cl$. Calculated %: Cl 24.51.

The data obtained gave a basis for assuming that the substance with a b.p. of 133-158° consisted of a mixture of the chloride 2,3-dimethyl-6-chlorohexene-3 with the hydrocarbon – trimethylcyclopropylethylene, which may be formed via the splitting off (under the influence of pyridine) of hydrogen chloride from the unstable cyclic chloride which is being formed, methylisopropylcyclopropylchloromethane.

Fraction with a b.p. of 168°: a colorless liquid with a sharp odor, it quickly decolorized a $KMnO_4$ solution; d_4^{20} 0.8859; n_D^{20} 1.4525; MR_D 44.74. $C_8H_{15}Cl$ F. Calculated 43.54.

0.1196 g substance: 0.2479 g AgCl. Found %: Cl 24.32. $C_8H_{15}Cl$ F. Calculated %: Cl 24.23.

Ozonization of the chloride with a b.p. of 168°. 2.5 g of the chloride in 40 ml of chloroform was taken for ozonization. After elimination of the solvent the ozonide was decomposed with water. The solution was neutralized with soda. The neutral products were steam distilled and treated with a solution of 2,4-dinitrophenylhydrazine. The precipitate obtained had a m.p. of 116°, (from alcohol), which agreed with that of methylisopropylketone. An ether extract was made from the acidified aqueous salt solution. After drying and distilling off the ether, the residue was vacuum distilled. The acid boiled at 112° (25 mm) and congealed in the receiving flask; m.p. 38-39°. A sample mixed with known β-chloropropionic acid gave no melting point depression.

SUMMARY

1. In the reaction of methyl-n-butylcyclopropylcarbinol with both dilute hydrochloric acid and with phosphorus trichloride in the presence of pyridine, an unsaturated primary chloride – 4-methyl-1-chlorooctene-3

and a cyclic hydrocarbon – 2-cyclopropylhexene-2 – are formed.

2. Methylisopropylcyclopropylcarbinol is converted by reaction with phosphorus trichloride in the presence of pyridine into the unsaturated primary chloride – 2,3-dimethyl-6-chlorohexene-3 with admixture of a hydrocarbon which may have a trimethylcyclopropylethylene structure.

3. Dimethylcyclopropylcarbinol upon reaction with phosphorus trichloride in the presence of pyridine yields two chlorides: a cyclic chloride – dimethylcyclopropylchloromethane and an unsaturated chloride – 2-methyl-5-chloropentene-2; the cyclic hydrocarbon isomerizes into the unsaturated in the presence of traces of moisture.

4. The preparation of dimethylcyclopropylchloromethane and its isomerization to 2-methyl-5-chloropentene-2 confirm the correctness of the mechanism earlier proposed by us for the reaction of tertiary alcohols of the cyclopropane series with hydrochloric acid.

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* See Consultants Bureau Translation, page 1553.

** See Consultants Bureau Translation, page 259.

THE REACTIONS OF CERTAIN AROMATIC COMPOUNDS OF MERCURY, TIN AND LEAD WITH CARBON TETRACHLORIDE

Yu. A. Oldekop and B. N. Moryganov

The reaction of carbon tetrachloride with mercury diphenylate, depending on the conditions, goes in various directions. The formation of chlorobenzene, hexachloroethane and phenylmercuric chloride proceeds by a photoreaction [1, 2]. The direction of the process is changed by initiating the reaction with the addition of benzoyl peroxide: phenylmercuric chloride and benzotrichloride are formed [3, 4]. Exactly the same sort of reaction proceeds upon heating the components above 200° [5]. It was well known that other organometallic compounds, such as $(C_6H_5)_4Sn$ and $(C_6H_5)_4Pb$, reacted with carbon tetrachloride on exposure to light analogously to mercury diphenylate [6].

Upon the reaction of benzoyl peroxide with tetraphenyl lead and tetraphenyl tin in carbon tetrachloride, there takes place the dearylization of the organometallic compound and in the reaction products is always found benzoic acid, though the production of the latter remains unexplained. With the object of clarifying this point in the present work we initiated the reaction by addition of acetyl peroxide. The appearance of benzoic acid in the hydrolysis products in this case would have indisputably indicated the formation of benzotrichloride at the expense of the phenyl organometallic compound. However, upon heating the above indicated lead and tin derivatives with carbon tetrachloride with the addition of acetyl peroxide, the reaction only proceeds between the acetyl peroxide and carbon tetrachloride, while the $(C_6H_5)_4Sn$ and $(C_6H_5)_4Pb$ are isolated unchanged from the reaction mixture.

On the other hand, we wished to verify the difference between the thermo- and photoreactions in the case of other aryl mercury derivatives. With this object we chose α-dinaphthylmercury. It is well known that in the photoreaction of α- and β-dinaphthylmercuries [7, 8] with carbon tetrachloride, naphthylmercury chloride, hexachloroethane, naphthalene and a resinous substance are formed. Formation of naphthalene and a resin is explained by disproportionation of the naphthyl radical, which did not react with carbon tetrachloride. It was also known that the naphthyl radicals obtained by decomposition of the naphthoyl peroxide in the carbon tetrachloride solution, reacted with it with formation of chloronaphthalene and naphthotrichloride [9].

During the progress of the thermal reaction of α-dinaphthylmercury with carbon tetrachloride, we observed that the process of splitting off the naphthyl radical proceeds considerably more readily than that of the phenyl radical. In the reaction products the formation was demonstrated of α-naphthotrichloride, α-naphthylmercuric chloride, naphthalene and a resinous substance. The reaction proceeds according to the equation

$$\alpha\text{-}(C_{10}H_7)_2Hg + CCl_4 \rightarrow \alpha\text{-}C_{10}H_7HgCl + \alpha\text{-}C_{10}H_7CCl_3.$$

Chloronaphthalene was not found in the reaction products.

Upon raising the temperature there takes place complete dearylization of the α-dinaphthylmercury with formation of mercuric chloride and calomel.

Thus, it may be assumed that the thermal reaction of carbon tetrachloride with aryl derivatives of mercury proceeds according to such a general equation as

$$Ar_2Hg + CCl_4 \rightarrow ArHgCl + ArCCl_3.$$

The direction of the thermal reaction is distinct from that of the photoreaction.

EXPERIMENTAL*

Reaction of acetyl peroxide with carbon tetrachloride in the presence of tetraphenyl tin. In a round-bottomed flask, supplied with a condenser with a ground joint and a dropping funnel, were mixed 10 g of tetraphenyl tin and 50 ml of carbon tetrachloride. The reaction mass was heated to the boiling point of carbon tetrachloride and through the dropping funnel, the drawn-out end of which was placed under the carbon tetrachloride layer, was introduced over 6 hours, 8.8 g of acetyl peroxide in 150 ml of carbon tetrachloride. After addition of the peroxide, heating was continued for 26 hours more. At the end of the heating, a test for peroxide gave a negative result. After distilling off the carbon tetrachloride on a water bath, the residue was steam distilled. Hexachloroethane in a quantity of 4.9 g with a m.p. of 186° was isolated, and gave no melting point depression in a mixture with pure hexachloroethane.

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* E. A. Sheer and A. Malysheva participated in the experimental work.

The residue after steam distillation consisted of tetraphenyl tin with a m.p. of 225°. A sample mixture with pure tetraphenyl tin melted at the same temperature. Its weight was equal to 9.43 g, or 94.3% of the starting quantity.

Reaction of acetyl peroxide with carbon tetrachloride in the presence of tetraphenyl lead: The reaction was conducted analogously to the experiment with tetraphenyl tin. 4.0 g of tetraphenyl lead and 4.0 g of acetyl peroxide were taken in 90 ml of carbon tetrachloride. The acetyl peroxide was slowly introduced in drops over 6 hours with subsequent heating for 20 hours. After completion of the reaction the filtered precipitate proved to be tetraphenyl lead with a m.p. of 225°. A sample mixed with pure tetraphenyl lead gave no melting point depression.

The total weight of the tetraphenyl lead recovered from the reaction was 3.7 g, or 92.5% of the initial amount. Hexachloroethane was separated from methanol; its weight was equal to 1.5 g.

Thermal reaction of α-dinaphthylmercury with carbon tetrachloride. The experiments were carried out by heating in an electric furnace 5.0 g of α-dinaphthylmercury and 30 ml of carbon tetrachloride in a sealed glass tube inserted in an iron tube. A thermometer was placed on the outside between the iron tube and the electric furnace. The duration of heating varied from 20 to 55 hours (see the table), the temperature was held in limits of 160 to 230°. Upon completion of the reaction, the tube was opened. The most intense resinification was observed at 230-235°. In experiments III and IV there was noticeable evolution of HCl. The precipitate was filtered off and washed with hot benzene. From the filtrate was isolated α-naphthylmercuric chloride; after repeated recrystallization from benzene it had a m.p. of 188°. No melting point depression was observed in a mixture with pure α-naphthylmercuric chloride. The part of the precipitate that was insoluble in benzene, consisting of mercuric chloride and calomel, was repeatedly washed with hot water and the divalent mercury ion was determined in the water by its conversion into HgS.

TABLE

Expt. No.	Temperature of the experiment	Duration of heating (hrs.)	Products of the reaction							
			α-naphthylmercuric chloride		calomel		mercuric chloride		naphthalene (g)	α-naphthoic acid (g)
			(g)	(%)	(g)	(%)	(g)	(%)		
I	150-160°	20	3.9	97.7	–	–	–	–	0.28	0.03
II	160-170	25	3.66	91.7	–	–	0.02	–	0.25	0.54
III	200-210	35	0.97	24.3	1.65	–	0.75	–	0.52	Qualitative
IV	230-235	55	0.35	8.7	6 g (together with resin)	–	0.23	–	0.15	Qualitative

The part of the precipitate remaining after removal of the mercuric chloride consisted of calomel. The filtrate obtained after isolating α-naphthylmercuric chloride, mercuric chloride and calomel, was rendered alkaline with NaOH and steam distilled. After distilling off the solvent, naphthalene with an m.p. of 80° collected in the condenser. A sample mixed with pure naphthalene melted at the very same temperature. The residue from the steam distillation was filtered off and subsequently acidified with a mineral acid; α-naphthoic acid with a m.p. of 160-161° was isolated. A sample mixture with pure α-naphthoic acid gave no depression of the melting point.

In conclusion, we express deep gratitude to Prof. G. A. Razuvaev for continuing interest and valuable assistance in the work.

SUMMARY

1. Acetyl peroxide does not initiate the reaction between phenyl derivatives of tin and lead and carbon tetrachloride.

2. During the thermal reaction of α-dinaphthylmercury with carbon tetrachloride in a sealed tube at 150° and higher, there takes place formation of α-naphthylmercuric chloride, naphthotrichloride and naphthalene. By raising the temperature to 200° and higher, complete dearylization of the α-dinaphthylmercury to mercuric chloride and calomel occurs.

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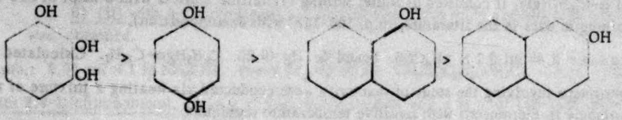
**** See Consultants Bureau Translation, page 2119.

REACTION OF ASYMMETRIC RHgR' MERCURY COMPOUNDS WITH PHENOLS

M. M. Koton and A. A. Bolshakova

One of us with his co-workers [1, 5] showed that aryl and alkyl compounds of mercury of the general formula R_2Hg are capable of mercurating phenols with formation of mono-, di- and trimercurated derivatives. It was of interest to study the behavior in reactions with phenols of asymmetric compounds of mercury containing radicals with varying reactivity in the Nesmeyanov and Kharasch series. With this object, the reactions of methyl-α-naphthylmercury (I), methylphenylmercury (II) and phenyl-α-naphthylmercury (III) with the following phenols were studied: 1) pyrogallol, 2) hydroquinone, 3) resorcinol, 4) p-cresol, 5) α-naphthol, 6) β-naphthol, 7) phenol, 8) p-nitrophenol, 9) m-nitrophenol, 10) 2,4-dinitrophenol, 11) 2,4,6-trinitrophenol, 12) p-bromophenol, 13) 2,4,6-tribromophenol, 14) p-chlorophenol, and 15) 2,4-dichlorophenol.

In the reaction of asymmetric compounds of mercury with unsubstituted phenols (including phenol), as in the case of symmetric mercury compounds, evolution of metallic mercury is observed with formation of the corresponding hydrocarbons. The following series of rates of evolution of metallic mercury from methyl-α-naphthylmercury upon heating with unsubstituted phenols for 9 hours at 100° was obtained



(31.3%) (26.8%) (22.2%) (6.3%)

The influence of the nature of the organic radicals entering into the composition of the asymmetric mercury compounds on the rate of the reaction with phenols was further studied. The following series in order of amount of mercury evolved was obtained for 6 hours heating at 100° of RHgR' with pyrogallol

$$C_6H_5Hg\alpha\text{-}C_{10}H_7 > CH_3Hg\alpha\text{-}C_{10}H_7 > CH_3HgC_6H_5$$

(54.8%) (24.9%) (22.2%)

These results were in excellent agreement with the position of the radicals in the Nesmeyanov-Kharasch series

$$\alpha\text{-}C_{10}H_7 > C_6H_5 > CH_3,$$

where the most electronegative appears to be $\alpha\text{-}C_{10}H_7$.

In the study of the reaction of RHgR' with substituted phenols it was shown that asymmetric compounds of mercury, just as the symmetric, can mercurate phenols with this difference: that the $RHg^{\cdot}$ enters into the phenol benzene ring containing the least reactive radical. Thus, in the reaction of phenols with $CH_3Hg\alpha\text{-}C_{10}H_7$ and $CH_3HgC_6H_5$ phenol derivatives are formed containing the $CH_3Hg^{\cdot}$ radical where the less reactive methyl radical is linked with the mercury atom, and the corresponding naphthalene or benzene is evolved. In the reactions of $C_6H_5Hg\alpha\text{-}C_{10}H_7$ with phenols phenol derivatives are formed containing the $C_6H_5Hg^{\cdot}$ radical, and naphthalene is evolved. On the basis of the reactions studied we consider it possible to assume the following free-radical mechanism (for example with methyl-α-naphthylmercury):

1) $CH_3Hg\alpha\text{-}C_{10}H_7 \longrightarrow CH_3Hg^{\cdot} + \alpha\text{-}C_{10}H_7^{\cdot}$,

2) $RC_6H_4OH + \alpha\text{-}C_{10}H_7^{\cdot} \longrightarrow C_{10}H_8 + {}^{\cdot}C_6H_3(OH)R$,

3) $CH_3Hg^{\cdot} + {}^{\cdot}C_6H_3(OH)R \longrightarrow CH_3HgC_6H_3(OH)R$.

In spite of the general character of the reactions of RHgR' with substituted phenols, differences were successfully established depending on: 1) the nature and number of substituents in the benzene ring of the phenol, and 2) the nature of the radicals linked with the mercury in RHgR'. Increasing number of nitrogroups in the phenol molecule lowers its reactivity, which is evident for example in $C_6H_5Hg\alpha\text{-}C_{10}H_7$, which gives with p-nitrophenol exclusively a dimercury derivative, with 2,4-dinitrophenol with gives mono- and dimercury derivatives, and with

2,4,6-trinitrophenols which give only a monomercury derivative.

A similar regularity is observed with accumulation of bromine in the phenol molecule. On the other hand, accumulation of hydroxy groups in phenols increases the reaction rate. With phenol there is formed a monomercury derivative, while with resorcinol – di- and trimercury derivatives.

In all cases of reactions of RHgR' with substituted phenols the most reactive compound appears to be $C_6H_5Hg\alpha\text{-}C_{10}H_7$ in comparison with $CH_3Hg\alpha\text{-}C_{10}H_7$ and $CH_3HgC_6H_5$.

EXPERIMENTAL

Methyl α-naphthylmercury was synthesized by the method of Freidlina, Nesmeyanov and Kocheskov [2], starting from CH_3HgI and $(\alpha\text{-}C_{10}H_7)_2SnCl_2$ with a yield of 50% of the theoretical. Methyl-α-naphthylmercury was obtained in the form of fine colorless shining crystals with a m.p. of 82° (84° according to the literature data).

0.0492 g sub.: 2.86 ml 0.1 N NH_4CNS. Found %: Hg 58.13. $CH_3Hg\alpha\text{-}C_{10}H_7$. Calculated %: Hg 58.55.

Methylphenylmercury was synthesized by the action of C_6H_5MgBr on CH_3HgI [3]. An attempt to obtain this compound by the action of CH_3MgI on C_6H_5HgBr gave a result that proved to be negative.

Methylphenylmercury was a heavy transparent liquid. In view of its instability, it was identified by conversion into the methyl mercury chloride, with a m.p. of 170-171°, a test mixture of which melted at 170° (m.p. 171° according to the literature).

Phenyl-α-naphthylmercury was obtained by the Kharasch and Marker method [4] by the reaction of C_6H_5MgBr and $\alpha\text{-}C_{10}H_7HgBr$; it consisted of white, shining crystalline leaflets with a m.p. of 110-112° with decomposition (according to data in the literature, m.p. 100-115° with decomposition).

0.0504 g sub.: 2.48 ml 0.1 N NH_4CNS. Found %: Hg 49.20. $C_6H_5Hg\alpha\text{-}C_{10}H_7$. Calculated %: Hg 49.59.

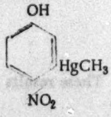
All experiments involving the study of reactivity were conducted via heating a mixture of the substance in a sealed glass ampoule in thermostats with sensitive temperature regulators.

Reaction of Methyl-α-naphthylmercury (I) and Methylphenylmercury (II) with Phenols

In all the experiments the batches of mercury compounds and phenols equaled 0.3 g, the temperature was 100 and 130° and the duration of the reaction was 3-6 hours. Naphthalene or benzene were observed to be evolved and were identified in the usual way.

1) (I) and (II) with p-Nitrophenol. The reaction mass was of a yellow color. After recrystallization from alcohol, 0.15 g of yellow crystals with a m.p. of 168-170° was isolated (a)

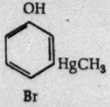
0.0500 g sub.: 2.83 ml 0.1 N NH_4CNS. Found %: Hg 56.60. $CH_3HgC_6H_3(OH)NO_2$. Calculated %: Hg 56.73.



(a)

The substance obtained was cleaved by the action of HCl in the cold (–10°) with formation of p-nitrophenol with a m.p. of 113-114°, a test mixture melted at 114°, and the methylmercuric chloride at 168-169°, a test mixture at 170° (170° according to the literature).

The compound obtained by treatment with bromine (in a solution of potassium bromide) was cleaved with formation of 3-bromo-4-nitrophenol with a m.p. of 128-129° (129-130° according to the literature). The Hg^{++} ion was formed in aqueous solution. The new compound obtained was, consequently, 3-methylmercuric-4-nitro-1-hydroxybenzene (a)



(b)

2) (I) and (II) with m-Nitrophenol. 0.18 g of yellow crystals with a m.p. of 126-127°, soluble in hot alcohol, was obtained.

0.0450 g sub.: 2.55 ml 0.1 N NH_4CNS. Found %: Hg 56.67. $CH_3HgC_6H_3(OH)NO_2$. Calculated %: Hg 56.73.

3) (II) with 2,4-Dinitrophenol. 0.15 g of a yellow crystalline substance was obtained with a m.p. of 99-102° after recrystallization from alcohol.

0.0500 g sub.: 2.505 ml 0.1 N NH_4CNS. Found %: Hg 50.10. $CH_3HgC_6H_2(OH)(NO_2)_2$. Calculated %: Hg 50.33.

4) (I) and (II) with 2,4,6-Trinitrophenol. 0.18 g of yellow crystals, soluble in alcohol, was obtained; m.p. 125-127°.

5) (I) and (II) with p-Bromophenol. 0.16 g of white shining crystals with a m.p. of 126-128° was isolated.

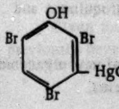
0.0550 g sub.: 2.84 ml 0.1 N NH_4CNS. Found %: Hg 51.63. $CH_3HgC_6H_3(OH)Br$. Calculated %: Hg 51.75.

The compound obtained was readily cleaved by an alcoholic solution of HCl with formation of p-bromophenol with a m.p. of 62-63°, a test mixture melted at 63°, and the methylmercuric chloride had a m.p. of 169-170°. By bromination of the substance obtained with bromine (in a solution of potassium bromide) 3,4-dibromophenol with a m.p. of 78-79° was isolated (78,79° in the literature). Thus, the substance obtained by us was 3-methylmercuric-4-bromo-1-hydroxybenzene. (b).

6) (I) and (II) with 2,4,6-Tribromophenol. 0.48 g of shiny crystals with a m.p. of 120-121° was obtained.

0.0720 g sub.: 2.63 ml 0.1 N NH_4CNS. Found %: Hg 36.51. $CH_3HgC_6H(OH)Br_3$. Calculated %: Hg 36.77.

The compound was cleaved by an alcoholic solution of HCl with formation of tribromophenol with a m.p. of 95-96°, a test mixture melted at 96°, and the methylmercuric chloride had a m.p. of 169-170°; a test mixture melted at 170°. By the action of bromine (in potassium bromide solution) 2,3,4,6-tetrabromophenol with a m.p. of 115-116° was isolated (m.p. 116,-113° according to the literature). Thus, the compound obtained by us consisted of 3-methylmercuric-2,4,6-tribromo-1-hydroxybenzene. (c).



(c)

7) (I) and (II) with Resorcinol. 0.1 g of an insoluble infusible substance with a light, rose color was isolated.

0.0500 g sub.: 3.70 ml 0.1 N NH_4CNS. Found %: Hg 74.00 $(CH_3Hg)_2C_6H_2(OH)_2$. Calculated %: Hg 74.40.

8) (II) with p-Chlorophenol. 0.12 g of fine white shiny crystals with a m.p. of 116-118° was obtained.

0.0600 g sub.: 2.91 ml 0.1 N NH_4CNS. Found %: Hg 58.20. $CH_3HgC_6H_3(OH)Cl$. Calculated %: Hg 58.47.

9) (II) with 2,4-Dichlorophenol. 0.14 g of fine, white crystals with a m.p. of 108-109°, soluble in alcohol, was obtained.

0.0488 g sub.: 2.59 ml 0.1 N NH_4CNS. Found %: Hg 53.07. $CH_3HgC_6H_2(OH)Cl_2$. Calculated %: Hg 53.12.

10) (I) and (II) with p-Cresol. 0.2 g of a white, crystalline substance with a m.p. of 124-126° was obtained.

0.0300 g sub.: 1.86 ml 0.1 N NH_4CNS. Found %: Hg 62.00. $CH_3HgC_6H_3(OH)CH_3$. Calculated %: Hg 62.18.

11) (II) with Phenol. 0.12 g of light yellow crystals, which after recrystallization from benzene had a m.p. of 190-110°, was obtained.

0.0500 g sub.: 3.24 ml 0.1 N NH_4CNS. Found %: Hg 64.80. $CH_3HgC_6H_4(OH)$. Calculated %: Hg 65.00.

Reaction of Phenyl-α-naphthylmercury (III) with Phenols

The batches of mercury compounds and phenols amounted to 0.3 g. The experiments were conducted at 100 and 130°, and lasted for 3-6 hours. Naphthalene was evolved in all cases.

12) (III) with p-Nitrophenol. 0.14 g of yellow crystals, insoluble and infusible up to 250°, was isolated.

0.0500 g sub.: 2.86 ml 0.1 N NH_4CNS. Found %: Hg 57.20. $(C_6H_5Hg)_2C_6H_2(OH)NO_2$. Calculated %: Hg 57.96. It was by alcoholic HCl cleaved with formation of p-nitrophenol, m.p. of 114°, (test mixture melted at 113-114°); the the phenylmercuric chloride had m.p. 250°, text mixture, m.p. 250°.

13) (III) with 2,4,6-Trinitrophenol. After recrystallization from alcohol 0.12 g of yellow crystals with a m.p. of 157° with decomposition was isolated.

0.0482 g sub.: 1.90 ml 0.1 N NH_4CNS. Found %: Hg 39.42. $C_6H_5HgC_6H(OH)(NO_2)_3$. Calculated %: Hg 39.67.

14) (III) with p-Bromophenol. 0.26 g of a white, insoluble and infusible substance was isolated.

0.1000 g sub.: 10.94 ml 0.05 N $Na_2S_2O_3$. Found %: Hg 54.70. $(C_6H_5Hg)_2C_6H_2(OH)Br$. Calculated %: Hg 55.25.

The substance was cleaved by alcoholic HCl with formation of p-bromophenol with a m.p. of 63-64°, a test mixture melted at 63°, and the phenylmercuric chloride had a m.p. of 250-251°, and a test mixture melted at 250°.

By the action of bromine (in potassium bromide solution) the substance was cleaved with formation of 2,4,6-tribromophenol with a m.p. of 90-92°, a test mixture melted at 92°. The compound obtained by us consisted of 2,6-diphenylmercury -4-bromo-1-hydroxybenzene [5].

15) (III) with 2,4,6-Tribromophenol. 0.16 g of a light, rose-colored, finely crystalline substance, with a m.p. of 174-175° with decomposition, was obtained.

0.0390 g sub.: 1.28 ml 0.1 N NH_4CNS. Found %: Hg 32.80. $C_6H_5HgC_6H(OH)Br_3$. Calculated %: Hg 33.08.

16) (III) with Resorcinol. 0.05 g of a reddish-brown crystalline substance with a m.p. of 132° (with decomposition), insoluble in organic solvents, was obtained.

0.035 g sub.: 2.11 ml 0.1 N NH_4CNS. Found %: Hg 60.28. $(C_6H_5Hg)_2C_6H_2(OH)_2$. Calculated %: Hg 60.40.

In ethyl alcohol (after 3 hours at 130°) 0.025 g of a dimercury compound and 0.555 g of dark-brown crystals which were insoluble and infusible were obtained.

0.0510 g sub.: 3.25 ml 0.1 N NH_4CNS. Found %: Hg 63.72. $(C_6H_5Hg)_3C_6H(OH)_2$. Calculated %: Hg 64.03.

SUMMARY

1. Asymmetric compounds of mercury of the RHgR' type upon reaction with pyrogallol, hydroquinone and naphthol are decomposed with deposition of metallic mercury and formation of RH and R'H.

2. Upon reaction of $CH_3Hg\alpha\text{-}C_{10}H_7$ and $CH_3HgC_6H_5$ with substituted phenols the formation of new organomercury compounds of the general formula $CH_3HgC_6H_3(OH)R'$ and also of benzene and naphthalene occurs.

3. A new series of methyl-α-naphthylmercury, methylphenylmercury, and phenyl-α-naphthylmercury derivatives with various phenols was described.

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* See Consultants Bureau Translation, page a-575.

** See Consultants Bureau Translation, page 703, 709.

*** See Consultants Bureau Translation, page 2171.

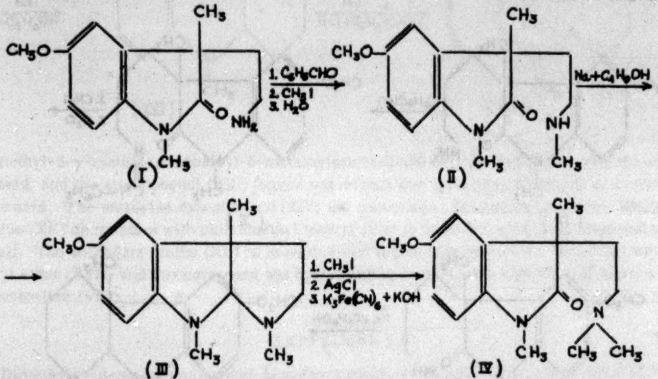
SYNTHETIC INVESTIGATIONS OF INDOLE DERIVATIVES

IV. THE SYNTHESIS OF ESERMETHOLE, HOMOESERMETHOLE, AND HOMOESEROLINE

M. M. Kolosov, L. I. Metreveli and N. A. Preobrazhensky

In investigating the relation between structure and physiological activity of any substance it is generally of very great interest to consider compounds only slightly different from the initial molecule, since greater variation in the structure ordinarily does not permit the influence of separate structural details to be determined. This is true, in particular, of the eserine-like compounds. Determination of the influence of configuration, and the dimensions of the second heterocyclic ring of the eserine molecule, on activity presents considerable theoretical interest. The simplest and most convenient method of studying this matter is to synthesize the racemic alkaloid and also its cyclo-homolog, and to compare the activity of the synthetic substance with the activity of natural eserine.

Given the preparation of racemic eserine, we accomplished the synthesis of d,l -esermethole (III), employing a previously developed method for closing the second heterocyclic ring of similar molecules [1].

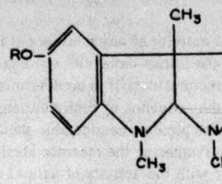


1,3-Dimethyl-3-β-aminoethyl-5-methoxyindolin -2-one (I) was converted into the iodomethylate of the benzylidene derivative which readily hydrolyzed in aqueous alcohol to the monomethyl amine,hydriodide (II). The amine by reduction with sodium and butanol gave, in excellent yield, a compound which did not react with acid chlorides and consequently was not a secondary amine.

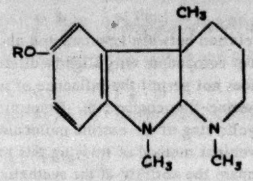
However, this substance (picrate m.p. 150°, picromethylate m.p. 175-177°), which we regarded as the racemic esermethol (III), differed from the methyl ester of racemic eseroline described in the literature (picrate m.p. 180-181°, picromethylate m.p. 183-184° and 192-193°) [2, 3]. Therefore, to prove its structure we subjected the chloromethylate of our esermethole to oxidation in alkaline medium. The dehydromethinated base isolated as a result of this proved to be identical with synthetic 1,3-dimethyl-3-β-dimethylaminoethyl-5-methoxyindolin-2-one (IV). Inasmuch as such a reaction sequence is characteristic of compounds possessing the eserine tricyclic system[4, 5], the structure of the d,l-esermethole synthesized by us evidently can be considered to be proved. It must be noted at the same time that the structure of the base obtained by the British investigators was not substantiated, and it can be assumed that it was not a tricyclic compound.

Actually, the previously described "d,l-esermethole" was prepared by methylation of noresermethole, obtained in turn by two distinct methods, and the bases synthesized by these methods were directly identified in the form of salts. However, it was subsequently shown experimentally for one of these synthetic methods that it did not lead to the formation of tricyclic compounds of the eserine series [6]. It ought to be noted in connection with the other synthetic method that noresermethole was obtained as a result of the hydrogenation of a cyclic amidine in conditions that did not exclude the possibility of reduction cleavage of the third ring (cf. [4]).

Just as in the synthesis of eserine (V) eseroline (VI) is a necessary starting material [7], to prepare the cyclohomolog of the natural alkaloid, homoeserine (VII), the presence of the corresponding phenol –homoeseroline (VIII) is required.

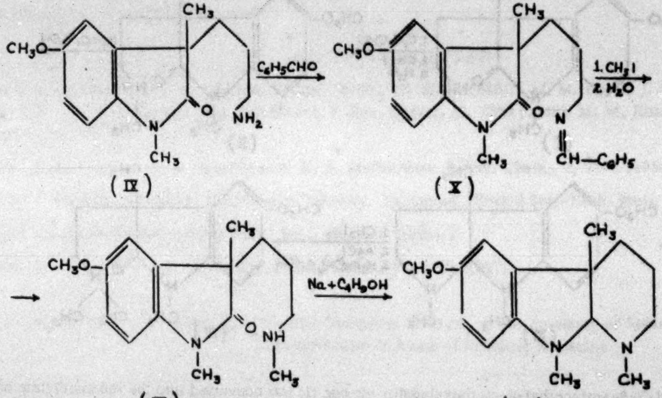


(V) R = CH_3NHCO
(VI) R = H

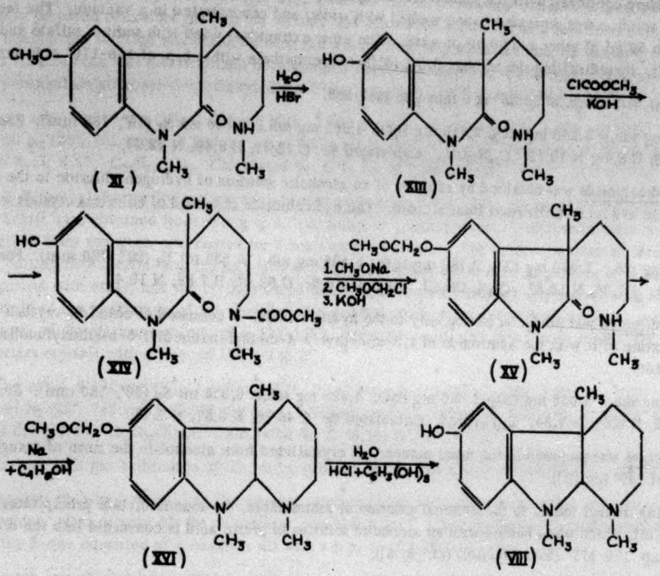


(VII) R = CH_3NHCO
(VIII) R = H

We proceeded to obtain the latter by way of hydrolysis of the methyl ether (XII) which was synthesized according to the scheme set forth below.



To hydrolyze homoesermethole (XII), the base or its hydrobromide was subjected to treatment with hydrobromic [8] or hydrochloric acid, and the concentration of acid, the temperature, and the length of heating were varied. However, it turned out that homoeseroline could not be successfully obtained by this method, since demethoxylation proceeded only under conditions which led to the formation of an inseparable mixture of substances. Attempts to cleave the ether bond of homoesermethole (XII) by heating it with aniline hydrochloride [9] or anhydrous aluminum chloride in gasoline (b.p. 70-77°) [10], were equally unsuccessful. Therefore, the synthesis of a more readily hydrolyzable derivative of homoeseroline was undertaken; the methoxymethyl ether (XVI) was chosen as such a compound, since it was, like all acetals, stable enough in alkaline, and readily decomposed in acidic media [11]. Thanks to this, it proved possible to conduct the hydrolysis under conditions in which homoeseroline (VIII) was formed without undergoing further changes, and under which it could be isolated.



1,3-Dimethyl-3-γ-methylaminopropyl-5-methoxyindolin-2-one (XI) was hydrolyzed with the aid of 50% hydrobromic acid, and the aminophenol (XIII) formed was treated with a calculated quantity of the methyl ester of chlorocarbonic acid. The urethylan thus obtained (XIV) was converted to the sodium phenolate, which gave the secondary amine (XV) on reaction with chloromethyl methyl ether in toluene and subsequent saponification with alcoholic alkali. The secondary amine (XV) on reduction with sodium and butanol was dehydrogenated to the methoxymethyl ether (XVI), and this compound was hydrolyzed by brief heating with phloroglucinol hydrochloride into the homoeseroline (VIII).

EXPERIMENTAL

I. 1,3-Dimethyl-3-β-methylaminoethyl-5-methoxyindolin-2-one (II). 11.5 g (1.00 mole) of 1,3-dimethyl-3-β-aminoethyl-5-methoxyindolin-2-one was mixed with 5.3 g (1.02 mole) of freshly distilled benzaldehyde; almost instantaneous evolution of heat occurred and the mixture became turbid from separation of water. After standing for 2 hours at room temperature, the reaction mass was heated 15 minutes on a water bath and the water evaporated off in a vacuum. To the residue was added 9 g (1.29 mole) of methyl iodide and the mixture was heated on a boiling water bath for 1 hour; another 2 g (0.29 mole) of methyl iodide was added, and the heating continued 1 hour more. Excess methyl iodide was driven off in a vacuum and 50 ml of 90% alcohol was added to the vitreous mass of iodomethylate formed; 35-40 ml of distillate was obtained at atmospheric pressure. A small quantity of ether was added to the solution obtained, and the crystalline precipitate was filtered off and washed with a mixture of alcohol and ether. The yield of the colorless hydriodide of 1,3-dimethyl-3-β-methylaminoethyl-5-methoxyindolin-2-one with a m.p. of 189-192° was 15.7 g (85%). After recrystallization from alcohol the substance had a m.p. of 198°; a mixture with the hydriodide of the starting primary amine melted at 160-165°.

2.890 mg sub.: 4.780 mg CO_2; 1.390 mg H_2O. 4.840 mg sub.: 0.333 ml N_2 (20°, 725 mm). 3.565 mg sub.: 0.245 ml N_2 (22°, 740 mm). Found %: C 45.10; H 5.38; N 7.64, 7.70. $C_{14}H_{21}O_2N_2I$. Calculated %: C 44.68; H 5.63; N 7.44.

The picrate was prepared from alcoholic solutions of the hydriodide and picric acid. After recrystallization from alcohol it consisted of yellow crystals with a m.p. of 178-179°.

II. Esermethole (III). 70 g (67 g-atom) of sodium was added, over a period of 10-15 minutes, to a boiling solution of 17.0 g (1 mole) of the hydriodide of 1,3-dimethyl-3-β-methylaminoethyl-5-methoxyindolin-2-one in

600 ml of absolute butyl alcohol. The reaction mass was heated on an oil bath for 2 hours, 300 ml of butanol was added and boiling continued until the sodium was completely dissolved. After cooling, 300 ml of water was added, the alcoholic solution was separated, twice washed with water, and concentrated in a vacuum. The residue was extracted with 50 ml of ether and 20 ml of water. The ether extract was dried with sodium sulfate and the solvent evaporated off. By redistilling the residue, 8.5 g (81%) of esermethole with a b.p. of 165-170° at 9 mm was obtained.

Material with a b.p. of 166.5° at 9 mm was analyzed.

3.100 mg sub.: 8.245 mg CO_2; 2.410 mg H_2O. 4.665 mg sub.: 0.500 ml N_2 (20°, 738 mm). Found %: C 72.53; H 8.70; N 12.12. $C_{14}H_{20}ON_2$. Calculated %: C 72.41; H 8.69; N 12.07.

The hydrochloride was obtained by addition of an alcoholic solution of hydrogen chloride to the ethereal solution of the base and recrystallization from alcohol. The hydrochloride consisted of colorless crystals with a m.p. of 190-191°.

3.065 mg sub.: 7.060 mg CO_2; 2.180 mg H_2O. 5.495 mg sub.: 0.530 ml N_2 (22°, 720 mm). Found %: C 62.81; H 7.96; N 10.57. $C_{14}H_{21}ON_2Cl$. Calculated %: C 62.57; H 7.88; N 10.43.

The hydriodide was produced analogously to the hydrochloride. It consisted of colorless crystals with a m.p. of 167°; a mixture of it with the hydriodide of 1,3-dimethyl-3-β-methylaminoethyl-5-methoxyindolin-2-one had a m.p. of 152-155°.

2.945 mg sub.: 5.035 mg CO_2; 1.480 mg H_2O. 4.425 mg sub.: 0.314 ml N_2 (20°, 730 mm). Found %: C 46.62; H 5.62; N 7.94. $C_{14}H_{21}ON_2I$. Calculated %: C 46.66; H 5.87; N 7.78.

The picrate was prepared in the usual manner. It crystallized from alcohol in the form of orange crystals with a m.p. of 150° (cf. [3]).

On adding methyl iodide to the ethereal solution of esermethole, the iodomethylate precipitates in the form of a colorless oil, which when heated with an alcoholic solution of picric acid is converted into the orange picromethylate, m.p. 175-177° (from alcohol) (cf. [2, 3]).

III. The relation of esermethole to acid chlorides. A. A mixture of 0.3 g (1.0 mole) of esermethole, 0.3 g (1.2 mole) of p-toluenesulfonic chlofide and 1 ml of dry pyridine was heated for 15 minutes on a water bath, cooled, and 1 ml of water added. The reaction mass was extracted with 10 ml of 10% aqueous potassium hydroxide and 20 ml of ether and the ethereal solution was washed with water and concentrated. The pyridine was driven off from the residue in a vacuum and an alcoholic solution of picric acid was added. The picrate which separated out had a m.p. of 149-150° after having been recrystallized twice from alcohol, and gave no melting point depression in a mixture with esermethole picrate.

B. 0.5 g (4.1 mole) of the methyl ester of chlorocarbonic acid and a solution of 0.5 g of potassium hydroxide in 2.5 ml of water were added to an ice-cooled solution of 0.3 g (1.0 mole) of esermethole in 1 ml of chloroform. The mixture was extracted for 3 minutes and poured into 10 ml of concentrated aqueous ammonia cooled to 0°. The base was extracted with ether, the extract was washed with water, dried with sodium sulfate and concentrated. The residue was converted by the usual method into the picrate, which after recrystallization from alcohol had a m.p. of 150° and gave no melting point depression in a mixture with esermethole picrate.

IV. Dehydroesermetholemethine (IV). 2.5 g (2.04 mole) of methyl iodide and, during the course of 1 hour, several drops of water, were added to a solution of 2.0 g (1.00 mole) of esermethole in 10 ml of absolute ether. The ethereal solution was decanted, the residue dissolved in 100 ml of 50% methanol and heated for 15 minutes on a water bath with freshly precipitated silver chloride (from 12 g of silver nitrate). The solution was filtered and concentrated in a vacuum, the residue was dissolved in 10 ml of alcohol, mixed with a solution of 5 g (1.75 mole) potassium ferricyanide and 7 g caustic potash in 60 ml water, and heated on a water bath for 3 minutes. After cooling, the base was extracted with ether, the extract dried and concentrated. To the residue was added 2 g of picric acid in 5 ml of alcohol, and the crystals which separated (1.3 g) were recrystallized from alcohol. The picrate obtained melted at 170-171°, and gave no melting point depression when mixed with the picrate of 1,3-dimethyl-3-β-dimethylaminoethyl-5-methoxyindolin -2-one.

0.6 of purified picrate was extracted with 10 ml of concentrated hydrochloric acid and the picric acid which separated out was extracted with ether. The aqueous solution was rendered alkaline with 20% sodium hydroxide and the base was extracted with ether. The extract was dried and concentrated and the residue was converted into the hydrochloride by the usual method. After recrystallization from alcohol it had a m.p. of 198-199° and gave no melting point depression in a mixture with the hydrochloride of 1,3-dimethyl-3-β-dimethylaminoethyl-5-methoxyindolin-2-one.

V. 1,3-Dimethyl-3-γ-benzalaminopropyl-5-methoxyindolin-2-one (X). To a solution of 39.0 g (1.00 mole) of 1,3-dimethyl-3-γ-aminopropyl-5-methoxyindolin-2-one in 115 ml of absolute benzene was added 17.0 g (1.02 mole) of freshly prepared benzaldehyde and the mixture was heated for a duration of 1 hour on a water bath. After having been cooled, the solution was decanted from the water which had separated and the benzene was distilled off in a vacuum. The residue was recrystallized from absolute methanol and washed with ether. The yield of 1,3-dimethyl-3-γ-benzalaminopropyl-5-methoxyindolin-2-one was 50.7 g (96%), m.p. 113.5-114.0°.

3.095 mg sub.: 8.500 mg CO_2; 1.925 mg H_2O. 3.000 mg sub.: 8.260 mg CO_2; 1.905 mg H_2O. 2.770 mg sub.: 0.206 ml N_2 (23°, 751 mm). 3.960 mg sub.: 0.294 ml N_2 (23°, 751 mm). Found %: C 74.89, 75.08; H 6.96, 7.10; N 8.47, 8.47. $C_{21}H_{24}O_2N_2$. Calculated %: C 74.96; H 7.20; N 8.33.

VI. 1,3-Dimethyl-3-γ-methylaminopropyl-5-methoxyindolin-2-one (XI). 25 ml of methyl iodide was added to the crude Schiff base obtained from 39.0 g of 1,3-dimethyl-3-γ-aminopropyl-5-methoxyindolin-2-one, and the mixture, shielded from moisture, was heated for 3 hours on a water bath. The reddish mixture obtained was dissolved in 105 ml of boiling 90% alcohol and the solvent was evaporated off as completely as possible on a water bath. The residue was ground with ether, and the crystals which precipitated were filtered off and washed with alcohol and ether. The yield of the hydriodide of 1,3-dimethyl-3-γ-methylaminopropyl-5-methoxyindolin-2-one was 54.0 g (88% on the basis of the primary amine), m.p. 148-152°. After recrystallizing twice from alcohol the substance consisted of colorless crystals with a m.p. of 156.0-156.5°.

3.040 mg sub.: 5.170 mg CO_2; 1.650 mg H_2O. 3.110 mg sub.: 5.265 mg CO_2; 1.615 mg H_2O. 3.685 mg sub.: 0.226 ml N_2 (25°, 745 mm). 3.790 mg sub.: 0.235 ml N_2 (25°, 745 mm). Found %: C 46.38, 46.17; H 6.07, 5.81; N 6.93, 7.03. $C_{15}H_{23}O_2N_2I$. Calculated %: C 46.14; H 5.94; N 7.17.

The mixture with the hydriodide of the initial primary amine had a m.p. of 146-149°.

The base was obtained by treating the aqueous solution of the hydriodide with potash and extracting with chloroform. The residue, after driving off the chloroform, was redistilled. 1,3-Dimethyl-3-γ-methylaminopropyl-5-methoxyindolin-2-one consisted of a colorless oil with a b.p. of 198-200° at 8 mm.

The picrate was obtained from the alcoholic solution of the base and picric acid. It crystallized from alcohol in the form of yellow crystals with a m.p. of 180.0-180.5°.

VII. Homoesermethole [1,9,11-trimethyl-6-methoxy-piperidino-(2,3-b)-indoline] (XII). 14.9 g (1.00 mole) of the hydriodide or 10.0 g (1.00 mole) of the base 1,3-dimethyl-3-γ-methylaminopropyl-5-methoxyindolin-2-one was reduced with 51 g (58 g-atoms) of sodium and 500 ml of absolute butyl alcohol exactly as described in the synthesis of esermethole. The residue after distilling off the butanol was dissolved in 100 ml of ether and the base extracted with dilute (1:3) hydrochloric acid (5 times with 10 ml). The acidic solution was rendered alkaline with a 10% solution of potassium hydroxide until it gave an alkaline reaction with phenolphthalein. The precipitate was filtered off, washed with water, dried in a vacuum and recrystallized from absolute ether with a dry ice-acetone freezing mixture. The yield of homoesermethole was 6.6 g (70%), m.p. 68-69°, b.p. 161-162° at 6 mm.

3.030 mg sub.: 8.150 mg CO_2; 2.400 mg H_2O. 2.975 mg sub.: 8.000 mg CO_2; 2.410 mg H_2O. 1.910 mg sub.: 0.196 ml N_2 (22°, 727 mm). 3.060 mg sub.: 0.313 ml N_2 (22°, 731 mm). Found %: C 73.36, 73.33; H 8.86, 9.06; N 11.36, 11.38. $C_{15}H_{22}ON_2$. Calculated %: C 73.12; H 9.01; N 11.37.

The hydriodide was obtained from an alcoholic solution of homoesermethole and hydrogen iodide and was precipitated with ether. After recrystallizing from alcohol it consisted of colorless crystals with a m.p. of 161.0-161.5°; a mixture with the hydriodide of 1,3-dimethyl-3-γ-methylaminopropyl-5-methoxyindolin-2-one had a m.p. of 145-147°.

3.020 mg sub.: 5.350 mg CO_2; 1.665 mg H_2O. 3.010 mg sub.: 5.330 mg CO_2; 1.660 mg H_2O. 4.950 mg sub.: 0.333 ml N_2 (22°, 732 mm). 5.465 mg sub.: 0.362 ml N_2 (22°, 732 mm). Found %: C 48.30, 48.28; H 6.17; N 7.50, 7.38. $C_{15}H_{23}ON_2I$. Calculated %: C 58.12; H 6.20; N 7.48.

The hydrobromide was obtained analogously to the hydriodide; it was crystallized from alcohol in the form of colorless crystals with a m.p. of 159.5-160.0°.

4.775 mg sub.: 0.353 ml N_2 (17°, 741 mm). 4.590 mg sub.: 0.343 ml N_2 (18°, 746 mm). Found %: N 8.49, 8.59. $C_{15}H_{23}ON_2Br$. Calculated %: N 8.56.

The picrate was obtained in alcoholic solution and recrystallized from alcohol. It consisted of bright red crystals with a m.p. of 146-147°.

VIII. 1,3-Dimethyl-3-γ-methylaminopropyl-5-hydroxyindolin-2-one (XIII). 37.7 g of the hydriodide of 1,3-dimethyl-3-γ-methylaminopropyl-5-methoxyindolin-2-one was heated in an atmosphere of nitrogen with 110 ml of 50% hydrobromic acid on a metal bath at 135-140° for 2 hours. The hydrobromic acid was distilled off in a vacuum, the residue was ground with alcohol and the crystals were filtered off and washed with alcohol. The mother liquor was concentrated and the residue was treated as described above. The yield of the hydrobromide of 1,3-dimethyl-3-γ-methylaminopropyl-5-hydroxyindolin-2-one was 31.7 g (99.6%). After recrystallization from water, the m.p. was 247-248°.

4.665 mg sub.: 0.354 ml N_2 (25°, 736 mm). 5.230 mg sub.: 0.395 ml N_2 (25°, 736 mm). Found %: N 8.43, 8.37. $C_{14}H_{21}O_2N_2Br$. Calculated %: N 8.51.

The picrate was obtained in aqueous solution from the hydrobromide and picric acid and recrystallized from alcohol. It consisted of yellow crystals with a m.p. of 206-207°.

IX. 1,3-Dimethyl-3-γ-(N-methyl-N-carbomethoxy)-amino-5-hydroxyindolin-2-one (XIV). 31.7 g (1.00 mole) of the hydrobromide of 1,3-dimethyl-3-γ-methylaminopropyl-5-hydroxyindolin-2-one was dissolved by being heated in 75 ml of water. The solution was quickly cooled to 5°, 10.0 g (1.10 mole) of the methyl ester of chlorocarbonic acid was added, and, during energetic stirring and cooling with a mixture of ice and salt, 110 ml of a 20% solution of potassium hydroxide was added at such a rate that the temperature did not rise above 5°. The non-phenolic substances were extracted with 50 ml of ether, the aqueous solution was acidified while being cooled, with concentrated hydrochloric acid until the reaction was acidic to Congo red. The oil which separated was extracted with chloroform (4 times with 50 ml). The extract was washed with a solution of sodium bicarbonate and water. After the extract was dried with sodium sulfate, the chloroform was distilled off, and the residue recrystallized from a mixture of ether and methanol. The yield of 1,3-dimethyl-3-γ-(N-methyl-N-carbomethoxy)-aminopropyl-5-hydroxyindolin-2-one was 24.7 g (84%), the m.p. was 115.5-116.5°, the b.p. was 225-226° at 0.35 mm.

3.700 mg sub.: 0.304 ml N_2 (23°, 740 mm). 3.575 mg sub.: 0.294 ml N_2 (22°, 742 mm). Found %: N 9.23, 9.29. $C_{16}H_{22}O_4N_2$. Calculated %: N 9.15.

X. Methoxymethyl ether of 1,3-dimethyl-3-γ-methylaminopropyl-5-hydroxyindolin-2-one (XV). A solution of 2.0 g (1.00 g-atom) of sodium in 20 ml of methanol was added to an ice cooled solution of 26.5 g (1.00 mole) of 1,3-dimethyl-3-γ-(N-methyl-N-carbomethoxy)-aminopropyl-5-hydroxyindolin-2-one in 40 ml of absolute methyl alcohol and the solvent was completely driven off in a vacuum in a stream of nitrogen. The residue was ground into a fine powder and suspended in 160 ml of absolute toluene. The mixture was cooled to −12° and while it was stirred, 6.25 g (0.90 mole) of hydrogen chloride-free chloromethyl ether was added to it. The reaction mass was held, while being stirred, for 20 minutes at a temperature of from −10 to −5°, for 1 hour 40 minutes at a temperature of from −5 to 0°, for 2 hours at 0-5°, for 4 hours at 5-10°, for 6 hours at 10-20° and was left at room temperature overnight. After this, 110 ml of a 5% solution of potassium hydroxide was added while the mixture was stirred, the toluene solution was separated, washed with water and concentrated in a vacuum. The combined aqueous solutions were extracted with 50 ml of ether and washed, and the dried extract was added to the residue after distilling off the toluene. After elimination of the ether and the residual toluene 20.3 g (67%) of the unpurified methoxymethyl ether of 1,3-dimethyl-3-γ-(N-methyl-N-carbomethoxy)-aminopropyl-5-hydroxyindolin-2-one was obtained. The substance was heated on a water bath for 3 hours with a solution of 14.3 g of potassium hydroxide in 53 ml of methanol. Subsequently the methanol was distilled off in a vacuum, 30 ml of water was added to the residue and the oil which separated was extracted with ether. The extract was washed with water, dried with sodium sulfate and concentrated. After the residue had been fractionally distilled twice, 12.2 g (72%) of the methoxymethyl ether of 1,3-dimethyl-3-γ-methylaminopropyl-5-hydroxyindolin-2-one with a b.p. of 186-193° at 1 mm was obtained.

A fraction with a b.p. of 184° at 1 mm was analyzed.

n_D^{24} 1.5335; d_{20}^{24} 1.1218; MR_D 80.91; calculated, 81.13.

3.485 mg sub.: 0.294 ml N_2 (24°, 731 mm). 3.225 mg sub.: 0.274 ml N_2(25°, 736 mm). Found %: N 9.31, 9.42. $C_{16}H_{24}O_3N_2$. Calculated %: N 9.51.

The picrate was obtained from an alcoholic solution of the amine and picric acid. After recrystallization from alcohol it consisted of yellow crystals with a m.p. of 140-141°.

XI. Methoxymethyl ether of homoeseroline [1,9,11-trimethyl-6-methoxymethoxy-piperidino-(2,3-b)-indoline] (XVI). 8.4 g (1 mole) of the methoxymethyl ether of 1,3-dimethyl-3-γ-methylaminopropyl-5-hydroxyindolin-2-one was reduced with 35 g (53 g-atoms) of sodium and 350 ml of butyl alcohol as was described in the synthesis of esermethole. 5.9 g (74%) of the methoxymethyl ether of homoeseroline with a b.p. of 143-145° at 1 mm (after redistilling twice) was obtained.

Material with a b.p. of 145° at 1 mm was analyzed.

n_D^{20} 1.5438; d_{20}^{20} 1.0964; MR_D 79.50; calculated, 79.25.

3.035 mg sub.: 0.284 ml N_2 (25°, 736 mm). 2.810 mg sub.: 0.255 ml N_2 (25°, 736 mm). 583 mg sub.: 295 mg formaldehydephloroglucide. Found %: N 10.38, 10.07; CH_2 5.14. $C_{16}H_{24}O_2N_2$. Calculated %: N 10.14; CH_2 5.07.

The picrate was obtained by the usual method and recrystallized from alcohol. It consisted of dark yellow crystals with a m.p. of 126.5-127.5° (with decomposition).

XII. Homoeseroline [1,9,11-trimethyl-6-hydroxypiperidino-(2,3-b)-indoline] (VIII). 0.798 g of the methoxymethyl ether of homoeseroline was heated for 40 minutes at 70-75° with 50 ml of phloroglucinol hydrochloride [12]; the reaction mass was cooled, and the precipitate of formaldehydephloroglucide was filtered off. Excess phloroglucinol was extracted from the filtrate with benzene and the acidic solution was concentrated in a vacuum. 5 ml of absolute alcohol was added to the residue and the solvent was distilled off in a vacuum; this operation was repeated 4-5 times, after which the residue was dried in a vacuum over potassium hydroxide to constant weight. The residue was then dissolved in a mixture of 25 ml of dry chloroform and 2 ml of absolute methanol, and a dry chloroform solution of ammonia was added until the ammonium chloride had completely precipitated. 75 ml of absolute ether was subsequently added, the solution was filtered and concentrated in a vacuum. The residue was redistilled at 0.02 mm and a bath temperature ranging up to 160°. 0.184 g (27%) of homoeseroline in the form of a slightly colored vitreous mass was obtained.

3.220 mg sub.: 8.560 mg CO_2; 2.360 mg H_2O. 2.905 mg sub.: 7.720 mg CO_2; 2.225 mg H_2O. 3.005 mg sub.: 7.990 mg CO_2; 2.270 mg H_2O. 2.995 mg sub.: 0.324 ml N_2 (29°, 736 mm). 3.045 mg sub.: 0.324 ml N_2 (19°, 736 mm). Found %: C 72.50, 72.48, 72.51; H 8.20, 8.57, 8.45; N 12.25, 12.05. $C_{14}H_{20}ON_2$. Calculated %: C 72.41; H 8.69; N 12.12.

SUMMARY

1. Racemic esermethole was synthesized and its structure was demonstrated by its conversion by exhaustive methylation and subsequent oxidation to dehydroesermetholmethine identical with synthetic 1,3-dimethyl-3-β-dimethylaminoethyl-5-methoxyindolin-2-one.

d,l-Esermethol was shown to be different from the compound described under that name by British investigators.

2. A method was developed for synthesizing homoesermethole and homoeseroline, the most important compound in the preparation of the homolog of eserine —homoeserine.

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REACTIONS OF THE LABILE AMINO GROUP

III. REDUCTION CLEAVAGE OF GRAMINE – A NEW SYNTHESIS OF SKATOLE

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β-(Dimethylaminomethyl)-indole, which has received the name gramine or donaxine, was found by H. Euler and his co-workers in germinating barley, and almost simultaneously was isolated by A. P. Orekhov and S. S. Norkina [1] from the leaves of the central Asiatic reed Arundo Donax.

For the study of the chemical nature of this new alkaloid, these investigators distilled it over zinc powder. H. Euler and co-workers [2] and also A. P. Orekhov and S. S. Norkina [3] demonstrated the consequent formation of skatole, characterized by its melting point and in the form of a picrate with satisfactory analytical data.

This fact itself demonstrated that the new alkaloid belonged to the series of indole derivatives. This reaction has not been employed to prepare skatole. The methods for preparing skatole described in the literature are either based on the cyclization or on the alkylation of indole.

The first synthesis of skatole was accomplished by E. Fischer. By heating to 180° equal quantities of the phenylhydrazone of propionaldehyde and anhydrous zinc chloride, skatole was obtained with a yield of 34% [4]. An improvement of this method appears to be the patented method [5], according to which the yield is raised to 90% if the reaction is carried out up to 200° in a solvent (solvent naphtha of neutral coal-tar oil).

A. E. Arbuzov and V. M. Tikhvinsky discovered a method for the catalytic cleavage of arylhydrazones, which leads in the case of the lower aldehydes to indole derivatives and of the higher aldehydes – to the formation of nitriles [6]. By the catalytic cleavage of the phenylhydrazone of propionaldehyde carried out at high temperature in the presence of an insignificant quantity of catalyst, these investigators obtained skatole with yields constituting in the case of cuprous chloride 61%, of platinic chloride 60%, and of zinc chloride 73-74% of the theoretical [7].

Of the methods of alkylating indole, that method merits greatest attention which consists of heating (in an autoclave at 210-220° indole-2-carboxylic acid or indole with excess sodium methylate in methanol solution. The yield of raw skatole constituted in the first case 63% and in the second (from indole) 71% [8, 9].

In spite of the fact that skatole is widely distributed as a product of the activity of the animal organism, being formed as a result of the bacterial decomposition of proteins and amino acids, it has found almost no application in chemical practice. Skatole has a limited application in perfumery [10]. It has been noted that skatole possesses physiological activity in relation to plants; this was established by experiments on the coleoptiles (sprouts) of oats [11].

In studying the various conversions of β-dimethylaminomethyl compounds – the cleavage reaction of the amino group in β-(dimethylaminomethyl)-indole (gramine) in particular – we found that during distillation of gramine with zinc powder, as had been described by H. Euler and co-workers and also by A. P. Orekhov and S. S. Norkina, skatole formation is observed.

However, if the distillation of gramine is carried out with a mixture of zinc powder and ammonium chloride in a vacuum at 20-30 mm, then skatole is obtained with a yield of 53%. This result induced us to seek more gentle conditions for the reduction cleavage of gramine. It was found as a result of a series of experiments that by the reduction of gramine with zinc powder in an alkaline medium in an alcohol-water solution and subsequent steam distillation, skatole is obtained with a yield approaching 66%.

It is of interest to note that reduction in an acidic medium under conditions excluding the polymerization of skatole does not lead to the desired result.

Thus, a new method for the preparation of skatole has been found. In connection with the availability of indole isolated from coal-tar resin, gramine becomes a fully available substance, inasmuch as the conversion of indole into gramine proceeds remarkably easily and with high yields [12]. The method found for the preparation of skatole from gramine consequently has preparative significance.

EXPERIMENTAL

1. Preparation of Skatole by way of Dry Distillation

A mixture of 3.5 g of gramine with a m.p. of 126-127°, 6 g of zinc powder and 4 g of ammonium chloride was stirred in a Claisen flask with a low side arm and carefully heated on an open flame in a vacuum at 20-30 mm. Distillation of skatole began before long and the skatole quickly crystallized in the receiving flask. The yield of raw product with a m.p. of 91-93° amounted to 1.4 g (53%).

2. Preparation of Skatole in Solution

8 g of gramine with a m.p. of 126-127° was dissolved in 160 ml of methanol and 20 g of sodium hydroxide in 160 ml of water was added to the solution. 16 g of zinc powder was gradually introduced in small portions into the stirred solution, which was heated to boiling, over a period of 2 hours. The mixture was then heated on a boiling water bath while being well stirred for 12 hours. After this, the methanol was distilled off by the use of a high fractionation column. Skatole was steam distilled from the residue (until the distillate appeared transparent). After the material had stood on ice for several hours, snow-white crystals of skatole formed, which were filtered off and dried in a desiccator over sulfuric acid.

The yield of raw product with a m.p. of 91-93° constituted 4 g (66%). After recrystallization from petroleum ether, the skatole melted at 93-94°. The picrate (from ethyl alcohol) had a m.p. of 173°. Literature data: 173-176° [3] and 172-173° [10].

SUMMARY

A new method of preparing skatole is described.

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PROPERTIES OF LIGNIN CHLORODERIVATIVES

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It is well known that a portion of the halogen in halogenated ligins is bound firmly and is retained after boiling with water and alkali, while the other part is readily eliminated under these conditions and also by heating chlorolignins and is even eliminated when they are preserved in an atmosphere of moist air.

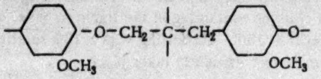
According to the data of L. P. Zherebov [1], the alcohol-soluble portion of the chlorolignin obtained by the chlorination of wood and containing 32% chlorine, loses half the chlorine merely on being dried. On boiling with dilute aqueous alkali for 5 hours, the chlorolignin containing 15.2% chlorine loses more than $^2/_3$ of its chlorine.

Powell and Whittaker [2] found that by treating chlorolignin with aqueous alkali, the chlorine content was reduced from 35% to 20.8%. Harris, Scherrer and Mitchell [3] also observed a significant loss of chlorine and bromine during treatment of halogenated lignins with alkaline solutions.

Chlorinated lignins, even those obtained by the chlorination of entirely insoluble forms of lignin, are dissolved in alkalis and alcohol, which indicates that some destruction of the lignin molecule occurs during chlorination.

Our knowledge concerning the chlorination of lignin and the properties of its chloroderivatives is, however, still very limited. The characteristic reactions and transformations of the chloroderivatives have not been studied. There are no systematic investigations which would serve to clarify the reaction mechanism of the chlorination of lignin and to establish the structure of the chloroderivatives.

Shorygina, Kefeli and Semechkina [4] showed that the structural units of lignin are linked to each other by ether bonds



Such a representation of the lignin structure may explain several properties of its chloroderivatives. M. F. Shostakovsky and co-workers have recently made an excellent study of the properties of vinyl ethers and their derivatives, including the properties of α-halogen substituted ethers and α,β-dihalogen substituted ethers [5]; the latter were also studied by M. N. Shchukina[6]. These investigations as well as the work of foreign scientists showed that β-halogen-substituted ethers are exceptionally unstable. Thus, α-methoxybenzylchloride is quantitatively hydrolyzed by being shaken with water for several seconds [7], forming benzaldehyde.

$$C_6H_5-CHClOCH_3 + H_2O \rightarrow C_6H_5CHO + CH_3OH + HCl.$$

Alkylchloroethyl ethers behave analogously

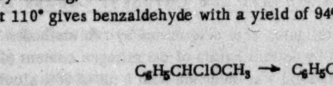
$$AlkOCHClCH_3 + H_2O \rightarrow CH_3CHO + AlkOH + HCl.$$

Aromatic α-halogen-substituted ethers RO−CHCl−Alk were somewhat more stable. α-Halogen-substituted ethers were decomposed by heating, with evolution of HCl and formation of an aldehyde [8]. For example, α-methoxybenzylchloride at 110° gives benzaldehyde with a yield of 94% of the theoretical and methyl chloride −91.7%.

$$C_6H_5CHClOCH_3 \rightarrow C_6H_5CHO + CH_3Cl.$$

The reaction proceeds partially with cleavage of HCl (1.9%). Pyridine cleaves HCl from α-chloroethyl ether with formation of vinylethyl ether [9].

N. N. Shorygina and A. A. Chuksanova established that in the chlorination of hydrolyzed lignin in a carbon tetrachloride chlorine solution without excess chlorine, at room temperature and in the absence of catalyst, the chlorine partially enters the aromatic nucleus in position 6 [10]. The exceptionally ready hydrolyzability and mobility of the other portion of the chlorine permits us to assume that at least part of the labile chlorine is found in the side chain of the lignin molecules in the α-position to the ether oxygen



Investigations conducted by us confirm what has just been said. We used technical hydrolyzed lignin from the Leningrad hydrolysis plant (see Communication 1) [11] as experimental material. The choice of material was made in view of the fact that hydrolyzed lignin, a multi-ton waste product of industry, had been little studied up to this time. Thorough study of this material is requisite for its rational utilization.

EXPERIMENTAL

The chlorolignins subjected to investigation were obtained from hydrolyzed lignin, chlorinated and purified of resin and dissolved hydrocarbons under mild conditions: at room temperature, in the dark, in the absence of catalyst. Samples were chlorinated in carbon tetrachloride and in water and contained about 5, 10, 20 and 25% chlorine [11].

Saponification of Chlorolignins

Batches of all the chlorolignin samples were boiled with water in a flask with a reflux condenser at a modulus of 1:100 for 1 hour. Upon completion of the boiling the lignin was filtered off from the acidic liquid, washed with water, dried initially in air and then over P_2O_5. In addition, all samples of chlorolignin were subjected to boiling for 1 hour with a reflux condenser also at a modulus of 1:100 with a 5% solution of NaOH. Upon completion of the boiling, sulfuric acid was added to the alkaline liquid (usually considerable and sometimes complete solution of the chlorolignins in the alkaline solution was observed) until the solution was acidic to Congo red, and the lignin was filtered off, washed and dried by the usual method.

Samples II and IV of the chlorolignins were saponified with 5% NaOH solution in the autoclave at 150° for 3 hours and with 10% solution of NaOH at 180° for 3 more hours. In both cases the modulus was 1:50.

On heating the chlorolignins with alkali under pressure, a profound change in the preparations was observed; they acquired a black color and considerable solubility in water. Only the water-insoluble fractions of these preparations were analyzed. The results obtained are set forth in Table 1, from which it is evident that by boiling with water for an hour the chlorolignins lose about 20% of their chlorine (samples I-III, when chlorinated in CCl_4, lose a smaller quantity of chlorine). Boiling with alkali evokes a more profound saponification; the quantity of saponified chlorine increases in proportion to the increase in its chlorolignin content. There is a noticeable tendency for the quantity of chlorine remaining in the lignin to level off. This is still more apparent in saponification with a 5% solution of NaOH at 150°. On boiling with a 10% solution of NaOH at 180°, partial saponification of the chlorine located in the nucleus evidently takes place.

The results obtained show that under the chosen chlorination conditions, entrance of stable chlorine into the lignin proceeds faster than that of labile chlorine, inasmuch as the highly chlorinated preparations contain a comparatively greater quantity of saponifiable chlorine than the slightly chlorinated preparations. Formation of new hydroxyl groups is observed during saponification in all cases. The quantity of hydroxyl groups in the chlorolignins and their saponification products was determined according to our modification of the Verley method. The more rigid the saponification conditions, the greater the number of newly originating OH groups arising in the saponification products; the preparations of chlorinated lignins saponified with alkali at 180° contain a considerably greater number of OH groups than the starting lignin. However, the quantity of OH groups appearing during the saponification does not exactly correspond with the quantity of chlorine saponified and in the majority of the cases is less than would result in theory. This indicates that the saponification does not proceed simply and that the nature of the chlorine in the chlorolignin side chain is different. The position and nature of the hydroxyl groups formed during the saponification of chlorolignin is still not clear.

Determination of the Content of Carbonyl and Carboxyl Groups in Chlorolignins

The carbonyl groups in lignin and chlorolignins were determined by two methods: by reduction of Fehling's solution (according to Bertrand's method) and by determination of the nitrogen content of the phenylhydrazones obtained from these lignin samples. 0.5 g of material was drenched with 5 ml of 96% alcohol and a solution of 1 g of phenylhydrazone hydrochloride and 1.5 g of sodium acetate in 10 ml of water was added to the mass obtained. The mixture was heated on a water bath for 30 minutes. After cooling the residue, we filtered and washed it with dilute hydrochloric acid and water until the acid reaction disappeared. The phenylhydrazone obtained was dried in a vacuum desiccator over P_2O_5 and its nitrogen content determined by Kjeldahl's method.

The quantity of carbonyl groups (according to Bertrand) was calculated from the weight of copper oxide formed. The results obtained by the two methods were comparatively close to each other and, therefore, in the majority of the experiments we limited ourselves to the Bertrand determination.

TABLE 1

Expt. No.	Preparation	Chlorine content (%)	OH content (%)	OCH_3 content (%)	>C=O content according to Bertrand's method (%)	>C=O content according to the nitrogen content of the phenylhydrazone (%)	COOH content (%)
1	Hydrolyzed lignin	–	7.83	9.00	3.33	2.58	1.41
2	Chlorolignin, No. II, chlorinated in CCl_4	10	6.53	7.30	4.47	4.18	2.84
3	The same after saponification with water for 1 hour	9.17	–	7.28	4.47	–	2.77
4	The same after saponification with 5% NaOH during boiling for 1 hour	7.69	9.8	7.89	–	–	4.71
5	The same after saponification with 5% NaOH at 150°	5.69	10.63	8.39	–	–	–
6	The same after saponification with 10% NaOH at 180°	4.98	–	8.69	–	–	–
7	Chlorolignin, No. III, chlorinated in CCl_4	19.53	6.56	–	4.09	–	5.54
8	The same after saponification with water	16.97	8.18	–	4.29	–	3.93
9	The same after saponification with 5% NaOH	12.43	9.33	–	4.48	–	6.99
10	Chlorolignin, No. IV, chlorinated in CCl_4	27.33	6.58	3.92	3.39	3.04	6.94
11	The same after saponification with water	22.28	7.39	4.06	3.98	4.21	5.93
12	The same after saponification with 5% NaOH while being boiled for 1 hour	12.55	9.44	4.19	4.03	3.99	8.73
13	The same after saponification with 5% NaOH at 150°	10.20	–	–	–	–	–
14	The same after saponification with 10% NaOH at 180°	6.53	12.84	–	–	–	–
15	Chlorolignin, No. II, chlorinated in water	12.40	6.47	4.62	6.13	–	5.67
16	The same, saponified with water	9.66	6.03	4.62	6.13	–	4.77
17	The same after saponification with 5% NaOH	6.50	8.59	4.89	6.66	–	–
18	The same after saponification with 5% NaOH at 150°	4.89	9.91	5.57	–	–	–
19	The same after saponification with 10% NaOH at 180°	2.62	11.68	5.50	–	–	–
20	Chlorolignin, No. IV, chlorinated in water	24.02	–	1.33	6.09	–	10.53
21	The same after saponification with water	19.46	–	1.40	7.32	–	9.65
22	The same after saponification with 5% NaOH while being boiled	8.20	–	1.34	6.98	–	–
23	The same after saponification with 5% NaOH at 150°	4.33	–	1.55	–	–	–
24	The same after saponification with 10% NaOH at 180°	3.30	12.04	–	–	–	–

TABLE 2

Preparation	Chlorine content (%)	OH content (%)	OCH_3 content (%)	>C=O content (%)	COOH content (%)
Hydrolyzed lignin	–	9.15	10.80	7.60	1.23
Chloroderivative, obtained by the chlorination of hydrolyzed lignin in CCl_4	18.82	9.01	9.45	5.29	3.59
Product of its saponification with water	14.01	–	–	7.33	2.81
Product of its saponification with 5% NaOH solution	10.40	9.95	–	7.50	5.95

The content of carboxyl groups was determined by the calcium acetate method. To batches of the chlorolignin (about 0.2 g) was added 20 ml of 0.5 normal calcium acetate solution and the mixture was left for 24 hours at room temperature in a small flask with a ground glass stopper. 20 ml of water was simultaneously poured into an exactly similar batch of chlorolignin which was also left for 24 hours under the very same conditions. At the end of the indicated period, both batches were filtered off and in each case 10 ml of the filtrate was titrated with 0.02 N NaOH solution. In the filtrate of the first batch, the acetic acid formed as a result of an exchange reaction between the calcium acetate and the carboxyl groups of the chlorolignin, and the hydrochloric acid partially cleaved off under these conditions were determined with phenolphthalein. In the filtrate of the second sample only the cleaved hydrochloric acid was determined by methyl orange. The quantity of carboxyl groups was calculated with a correction factor for the quantity of NaOH solution consumed in the titration of the hydrochloric acid formed. A simultaneous control titration was conducted with 20 ml of calcium acetate.

It is evident from the data of Table 1 that during chlorination in carbon tetrachloride, the quantity of carbonyl groups is insignificantly augmented. During chlorination in an aqueous suspension of lignin the quantity of carbonyl groups in the lignin is markedly increased.

During the saponification of chlorolignins the content of carbonyl groups is also somewhat increased. The content of carboxyl groups is significantly increased in proportion to the increase in chlorine content in the chlorolignins. This quantity is increased still more by saponification of the chlorolignins with alkali. A particularly great quantity of carboxyl groups in the chlorolignins is obtained by chlorination in water (evidently as a result of oxidation). The content of carboxyl groups is increased even more during saponification of the chlorolignins with alkali.

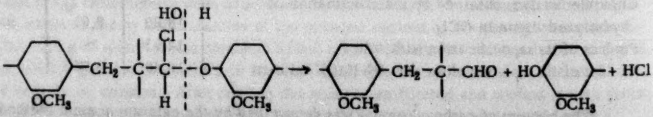
A more graphic change in the content of functional groups during the chlorination and saponification of chloroderivatives is noted in the case of hydrolyzed lignin chlorinated by a carbon tetrachloride chlorine solution and saponified with dry carbon tetrachloride that is kept moisture free.

The chlorolignin contained fewer carbonyl groups that the starting lignin, but its content of carboxyl groups was correspondingly greater. After saponification in water, the content of carbonyl groups in the product considerably increased and after alkaline saponification, the content of carboxyl groups very considerably increased (Table 2).

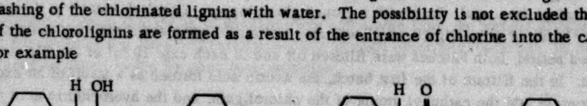
TABLE 3

Expt. No.	Preparation	Chlorine content (%)	>C=O content (%)	OH content (%)	Quantity of H_2 adsorbed (in % of weight of lignin)	Quantity of H_2 (in % of weight of lignin) required for the reduction of the carbonyl groups present	Quantity of H_2 (in % of weight of lignin) which adds to the double bond	Number of structural units per one double bond
1	Hydrolyzed lignin	–	3.33	7.83	0.2451	0.2378	0.0076	146
2	Chlorolignin, obtained by chlorination in carbon tetrachloride	19.53	4.08	6.56	0.2947	0.2926	0.0021	480
3	The same after treatment with pyridine for 15 hours at 20°	13.72	3.50	7.01	0.3980 0.4076	0.2303 0.2303	0.1677 0.1773	6.02 5.5
4	The same as in Experiment 2, after boiling with pyridine for 1 hour	11.28	3.16	7.02	0.3724	0.2276	0.1448	6.9

The increase in the content of carbonyl and carboxyl groups during the saponification of chlorolignins is accompanied by an increase in the content of hydroxyl groups. It appears to us that this phenomenon may be explained by a partial destruction of the chlorolignin molecule



It is probable that such partial destruction takes place even during the chlorination of lignin in aqueous media and also during the washing of the chlorinated lignins with water. The possibility is not excluded that a portion of the carbonyl groups of the chlorolignins are formed as a result of the entrance of chlorine into the carbon containing the hydroxyl group, for example



However, during hydrogenation in alkaline medium it was found that hydrolyzed lignin contained a very insignificant quantity of double bonds. Consequently, chlorination according to this scheme can proceed only to a very limited extent.

During saponification by alkali with heating, acid may be formed as a result of the Cannizzaro reaction.

It is characteristic that during the hydrolysis of chlorolignins with water, the content of carboxyl groups in all cases is not only not increased, but even is diminished, probably as a consequence of the partial splitting off of carboxyl groups during heating in an acidic medium.

Reaction of Chlorolignins with Pyridine

Chlorolignin samples (0.5 g) were heated on a water bath for 15 minutes with 5 mg of dry pyridine. Upon completion of the heating and after cooling in a small flask, water (50 mg) was added and the mixture was titrated with a 0.1 N solution of NaOH, using thymol blue as the indicator and removing drops on indicator paper. Both during heating under the indicated conditions and during standing with pyridine for 15 hours at 20°, the chlorolignins split off HCl. No increase in the content of hydroxyl groups during treatment of the chlorolignins with pyridine was observed. Comparative hydrogenation of the chlorolignins in the presence of Raney nickel at room temperature in a 2% alkaline solution before and after treatment with pyridine showed that pyridine splits off hydrogen chloride from chlorolignin with formation of a double bond. During the hydrogenation under the indicated conditions, reduction of the carbonyl groups takes place, which was demonstrated by the hydrogenation of unchlorinated hydrolyzed lignin. The quantity of hydrogen consumed in the hydrogenation of hydrolyzed lignin and also of chlorolignin (untreated with pyridine) corresponds exactly with that calculated for the reduction of the carbonyl groups contained in these lignins. The data are presented in Table 3.

SUMMARY

1. Under mild chlorination conditions (without catalyst at 10-12° and in the dark) firmly bound chlorine enters the lignin molecule faster than labile chlorine. Slightly chlorinated lignins primarily contain stable chlorine. Highly chlorinated lignins chiefly contain labile chlorine.

2. During saponification of chlorolignins with water and alkali, an increase in the content of hydroxyl groups takes place. A particularly sharp increase in the content of hydroxyl groups is observed during saponification with alkali at 150° and 180°. Under these conditions a significant part of the lignin is converted into a water-soluble form.

3. The content of carbonyl groups in lignin is insignificantly increased during chlorination in carbon tetrachloride, and sharply raised during chlorination in water.

4. The content of carboxyl groups is significantly increased in proportion to increase in the quantity of chlorine in the chlorolignins. The chlorolignins chlorinated in water contain an especially large number of carboxyl groups.

5. During saponification of chlorolignins with alkali, the content of carbonyl and particularly of carboxyl groups is increased. During saponification with water, a certain increase in the number of carbonyl groups is also observed. This is particularly noticeable in the chlorolignin preparation obtained under completely anhydrous conditions. During boiling of the chlorolignins with water, the content of carboxyl groups is evidently diminished by the splitting off of carbonic acid.

6. A hypothesis was presented concerning the possible mechanism of the hydrolysis of chlorolignins.

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THIOSEMICARBAZONES OF ALDEHYDES AND KETONES

III. THIOSEMICARBAZONES OF THE METHYL KETONES OF 3-ACETAMINOPHENOL

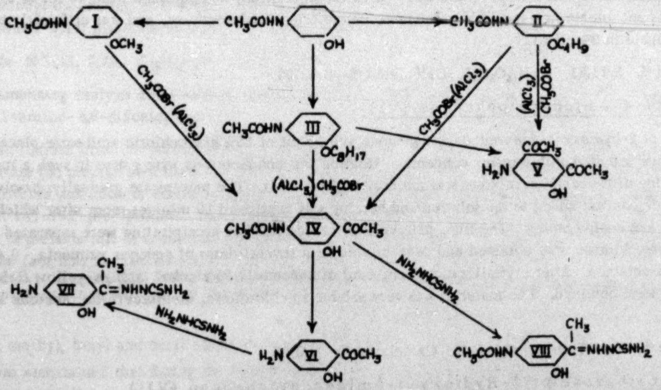
I. Kh. Feldman and A. A. Simeonov

In a continuation of the work on the preparation of thiosemicarbazones of aldehydes and ketones begun by one of us [1, 2], we prepared thiosemicarbazones of methyl ketones of phenols. There are hints in the literature concerning a weak tuberculostatic activity of the thiosemicarbazones of these ketones [3], but a recently published work has cast doubt on this [4].

Of the methods of obtaining the methyl ketones of the aromatic series described in the literature, the most suitable appeared to us to be the reaction of an acid halide (acetyl bromide) on phenol in the presence of anhydrous aluminum chloride.

This method was employed by Kunkel [5] to introduce a ketone group into acetanilide and in a number of other cases. The addition carried out by Behn [6], which facilitates the introduction of a ketone into aromatic phenols and nitrocompounds, was of practical use, although not in all cases.

For the synthesis of methyl ketones we prepared 3-acetaminophenol according to Izmailslky's directions [7], and prepared three ethers of this phenol – the methyl, n-butyl and n-propyl (I, II, III). It turned out that under the reaction conditions of the preparation of methyl ketones from these ethers according to the method indicated above, the alkyl ethers found in the ortho-position to the introduced ketone were saponified, while the acetamino groups in the para-position to the indicated ketone remained unchanged, and we obtained the methyl ketone of the unetherified acetaminophenol (IV) in all three reactions.



In our experiments, the reaction of introducing an acetyl group in m-acetanisidine (I) resulted in the isolation of only one substance – 2-hydroxy-4-acetaminoacetophenone (IV), which was obtained also in two other reactions; however, during the introduction of the acetyl group into two other ethers (II) and (III), one and the same substance was still obtained from both ethers. The solubility of this substance (V) in dilute alkali and dilute acid as well as elemental analysis showed that in it not only the alkoxy, but also the acetyl groups are saponified. In view of this, its structure may be considered to be that of 3-amino-4,6-diacetophenol.

The ketone (IV) was saponified and from it was obtained 2-hydroxy-4-aminoacetophenone (VI); the thiosemicarbazones (VII and VIII) of both ketones (IV and VI) were also obtained.

EXPERIMENTAL

2-Hydroxy-4-acetaminoacetophenone (IV)

8 g of m-acetanisidine, 12.7 g of acetyl bromide and 40 ml of preliminarily dried carbon disulfide were placed in a three-necked flask of 200 ml capacity supplied with a mechanical stirrer with a mercury seal and a reflux condenser with a sealed-in calcium chloride tube. The temperature of the solution being formed rose to 40-50°, while the solution was being stirred, and a precipitate quickly separated. For 25 minutes after this, aluminum chloride (20 g) was added to the stirred reaction mixture in small portions. In the beginning of the addition, a precipitate of the catalyst in the flask dissolved and the solution assumed a brownish red color and somewhat later began to separate into layers; the upper layer (carbon disulfide) had an orange-yellow color, the lower layer – more viscous and with a dark red color, gradually solidified. The reaction flask was heated on a bath to 40-50° in such a fashion that the upper layer (carbon disulfide) of the reaction mixture gently boiled for 1.5 hours. Upon completion of the reaction, the mass was cooled, the carbon disulfide poured off from the thick, dark brown precipitate and the precipitate was transferred to 200 g of chopped ice and left overnight. On the following day, the flocculant precipitate was filtered off, washed with 90 ml of water, and thoroughly pressed out, after which, in order to decompose the aluminum chloride complex, the precipitate was transferred to a 3% solution of hydrochloric acid (200 ml) and heated a short time on a boiling water bath. The bright ocher precipitate was separated, washed in two stages with 60 ml of water and thoroughly dried. 6.2 g of material was obtained (66%), which crystallized from alcohol with added carbon; we obtained white crystals with a m.p. of 142-144°, insoluble in ether, slightly soluble in boiling benzene, partially in boiling water, very soluble in alcohol, pyridine and in 3% alkali.

Found %: N 7.05, 7.23. $C_{10}H_{11}O_3N$. Calculated %: N 7.25.

Thiosemicarbazone of 2-Hydroxy-4-acetaminoacetophenone (VIII)

2 g of 2-hydroxy-4-acetaminoacetophenone and 15 ml of strong alcohol were placed in a three-necked flask supplied with a mechanical stirrer, a reflux condenser and a water bath. A solution of 1 g of thiosemicarbazide in 6 ml of almost-boiling water was added at a temperature of 55-60° and while the contents of the flask were being stirred; a yellow-rose solution formed which gradually became light yellow. The entire reaction was carried out in a period of 3 hours at 80-85°. On the following day, the precipitate was washed with a small quantity of water heated to 85° to free it of excess thiosemicarbazide. The yield was 22 g (80%) of pale yellow crystals. A white crystalline precipitate with a m.p. of 250-251° (with decomposition) was obtained from 40 ml of alcohol. The material was not soluble in water, ether, benzene, chloroform, dichloroethane, and was difficultly soluble in alcohol and very soluble in 3% alkali.

Found %: S 11.81. $C_{11}H_{14}O_2N_4S$. Calculated %: S 12.03.

2-Hydroxy-4-aminoacetophenone (VI)

1.0 g of 2-hydroxy-4-acetaminoacetophenone and 15 ml of 15% hydrochloric acid were placed in a round-bottomed flask supplied with a reflux condenser. Heating was conducted on wire gauze in such a manner that regular boiling of the reaction mixture was maintained for 1 hour. The precipitate gradually dissolved; a small quantity of carbon was added to the solution and heating was continued 10 minutes more, after which the solution was filtered and cooled on ice. The fine, pale yellow, curved needles precipitating were separated and dried. 0.63 g of hydrochloride was obtained and was treated with several drops of aqueous ammonia. 0.47 g (~60%) of base was obtained. After crystallization from 4 ml of aqueous (1:9) alcohol, orange-yellow flakes with a m.p. of 135-136° were obtained. The material was very soluble in chloroform, dichloroethane, acetone and boiling water.

Found %: N 9.17, 9.24. $C_8H_9O_2N$. Calculated %: N 9.26.

Thiosemicarbazone of 2-Hydroxy-4-aminoacetophenone (VII)

This thiosemicarbazone was obtained under the very same conditions as the thiosemicarbazone (VIII). 4.1 g of 2-hydroxy-4-aminoacetophenone in 30 ml of alcohol, a boiling solution of 2.5 g of thiosemicarbazone in 15 ml of water and 5 drops of strong hydrochloric acid were taken for reaction. 6.25 g of yellow crystals of a mixture of the base and its hydrochloride was obtained; the yield was almost equal to the theoretical. The precipitate was treated with several ml of aqueous ammonia, filtered off and recrystallized from alcohol. Pale yellow crystals with a m.p. of 193° (with decomposition) were obtained. They were insoluble in benzene, toluene, petroleum ether, chloroform, dichloroethane and ether, difficultly soluble even during heating in water and alcohol, more readily soluble in acetone.

Found %: S 14.20. $C_9H_{12}ON_4S$. Calculated %: S 14.29.

3-Acetylaminobutoxybenzene (II)

A solution of 6.6 g of sodium hydroxide in 200 ml of alcohol, 25 g of m-acetylaminophenol and 25 g of butyl bromide (20% excess) were placed in a 500 ml three-necked flask equipped with a mechanical stirrer with a mercury seal and with a reflux condenser. The mixture was heated to 80° on a water bath for 5 hours while being stirred. After this, the solution was filtered off from the small precipitate,which chiefly consisted of sodium bromide and poured into 1200 ml of water. A flocculant white precipitate was formed which was filtered off, washed with water, pressed and dried; its weight was 31 g (90%). After crystallization from 70° alcohol (1:5) shiny white flakes with a m.p. of 75-76° were obtained. The substance was very soluble in alcohols, chloroform, dichloroethane, ether, benzene, toluene, insoluble in petroleum ether and water.

Found %: N 6.42, 6.63. $C_{12}H_{17}O_2N$. Calculated %: N 6.75.

3-Acetylaminooctooxybenzene (III)

The substance was obtained in exactly the same way as 3-acetylaminobutoxybenzene. A solution of 5.3 g of sodium hydroxide in 120 ml of alcohol, 20 g of acetaminophenol and 26 g of octyl bromide were taken for reaction. Heating at 80° and stirring were continued for 7 hours; after the sodium bromide was separated, the filtrate was poured out in water. The emulsion formed was gradually converted on standing into a cream-colored precipitate. The latter was filtered off and dried; its weight was 32 g (92%). The material dissolved in 70° alcohol with carbon. The white, greasy-to-the-touch crystals obtained were collected in microscopic clusters of flakes with a m.p. of 57-58°; and were very soluble in ether, alcohols, acetone, chloroform, benzene, toluene, and insoluble in water and petroleum ether.

Found %: N 5.19. $C_{16}H_{25}O_2N$. Calculated %: N 5.31.

The introduction of the acetyl group into 3-acetaminobutoxybenzene (II) was conducted in exactly the same way as the introduction of the ketone group into 3-acetanisidine. 21 g of 3-acetaminobutoxybenzene were taken, dried, and distilled with 100 ml of carbon disulfide and 25 ml of acetyl bromide. After this when the stirrer had been started and the 3-acetylaminobutoxybenzene had been dissolved, anhydrous aluminum chloride was added. 18.75 g of air-dry technical product was isolated which was crystallized from 200 ml of alcohol with carbon added. A white crystalline precipitate (A) with a weight of 2.07 g was obtained. By repeated purification from alcohol crystals were obtained having the appearance under the microscope of truncated pyramids and with a m.p. of 253-253.5°; very soluble on heating in acetone, chloroform and dichloroethane and alcohols; soluble in 3% alkali and dilute hydrochloric acid; insoluble in water, ether and petroleum ether.

Found %: N 7.11, 7.15. $C_{10}H_{11}O_3N$. Calculated %: N 7.25.

The elementary analysis and solubility of the substance in alkali and acid demonstrated that the substance obtained was 3-amino-4,6-diacetophenol (V).

After the filtrate from the precipitate (A) had been diluted with a 5-fold quantity of water, 11.25 g of a rose-cream precipitate (B) precipitated from it. This was dissolved by being heated in 50 ml of alcohol with carbon; the solution was filtered and cooled; during its dilution with a 5-fold quantity of water, long, shiny, light-cream needles with a m.p. of 141-142° precipitated. The solubility in alkali, insolubility in acid, its elementary analysis, and the melting point depression test in a mixture with previously prepared 2-hydroxy-4-acetylaminoacetophenone (IV), were evidence of the fact that the two substances were identical. The experiment to introduce the acetyl group into 3-acetylaminooctoxy-benzene (III) led to the same results as the reaction of introduction of the acetyl group into 3-acetylaminobutoxybenzene (II), i.e., to substances (IV) and (V).

SUMMARY

1. The methyl, butyl and octyl ethers of 3-acetaminophenol (compounds I, II, and III) were prepared.

2. It was ascertained that during the introduction of the acetyl group into the indicated ethers in the para-position to the acetamino group with the aid of acetyl bromide (in the presence of aluminum trichloride), saponification of the ethers proceeds and one single product is obtained in all cases: 2-hydroxy-4-acetaminoacetophenone (IV); that is, the alkyl residue in the ortho-position is saponified, but the acetyl group in the para-position to the methyl ketone remains.

3. In the same reaction for the introduction of the methyl ketone group into the butyl and octyl ethers (II and III), a second product, 3-amino-4,6-diacetaminophenol (V), containing two acetyl groups is simultaneously obtained; in this case, the acetyl group in position 3 is saponified. Thus, it was demonstrated that in the given reaction, saponification of the group in the ortho-position to the introduced methyl ketone occurs, while the group in the para-position is not saponified.

4. Two thiosemicarbazones (VII and VIII) of the monomethylketones (IV and VI) were prepared.

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* See Consultants Bureau Translation, page 453.

XLII. CONTACT CONVERSIONS OF THE OXIDES OF TRIMETHYLENE AND OF TRIMETHYLENEGLYCOL

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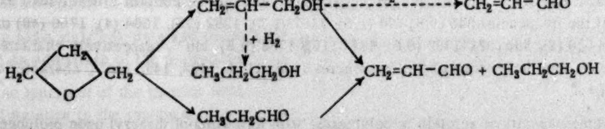
In our previous work on the contact conversions of four-membered cyclic sulfides it was demonstrated that trimethylene sulfide in contact with aluminum oxide at 350° in an atmosphere of hydrogen sulfide forms a five-membered cyclic disulfide – 1,2-dithiolane [1], and along with this undergoes considerable decomposition, which is even more intense in the absence of hydrogen sulfide.

α-Methyltrimethylenesulfide is isomerized under these same conditions with enlargement of the ring and formation of a cyclic monosulfide – tetramethylene sulfide (tetrahydrothiophene, thiophene) [2], and in the absence of hydrogen sulfide the degree of isomerization is increased. Along with isomerization into the tetramethylenesulfide, very considerable decomposition of the α-methyltrimethylenesulfide also occurs.

It might be expected that trimethylene oxide, with less stability than the trimethylenesulfide, would decompose during contact with aluminum oxide to an even greater extent and that the products of its contact conversion would be obtained in insignificant quantities. Inasmuch as the complete analogy in the behavior of ethylene oxide and ethylene glycol during their passage over aluminum oxide had been established earlier [3], we preliminarily studied the behavior of trimethyleneglycol under analogous conditions, and established that the products of its contact conversion were propionaldehyde, acrolein, propyl and allyl alcohols, ditrimethyleneglycol and α-methyl-β-ethylacrolein [4]. We assumed that the formation of all these compounds was a result of the dehydration of trimethyleneglycol with formation of allyl alcohol and trimethylene oxide, which instantly gave rise to propionaldehyde and compounds of its further transformation.

In the present work, the behavior of trimethylene oxide during contact with aluminum oxide both in the absence and in the presence of hydrogen sulfide was studied. It was established that in the absence of hydrogen sulfide, a mixture of reaction products was formed from which were isolated propionaldehyde and acrolein and also propyl and allyl alcohols, i.e., the very same compounds as were obtained by the dehydration of trimethyleneglycol under analogous conditions. In this connection, we proposed the same scheme for the mechanism of formation of these compounds as we had postulated for the contact dehydration of trimethyleneglycol, where the possible intermediate formation of trimethylene oxide was assumed: trimethylene oxide isomerizes into propionaldehyde and allyl alcohol, the latter as a result of disproportionation of the hydrogen is converted into propyl alcohol and acrolein. However, it is more probable that propyl alcohol and acrolein are formed as a result of disproportionation of hydrogen between allyl alcohol and propionaldehyde similarly to the way this occurs with ethyl alcohol and acrolein [5].

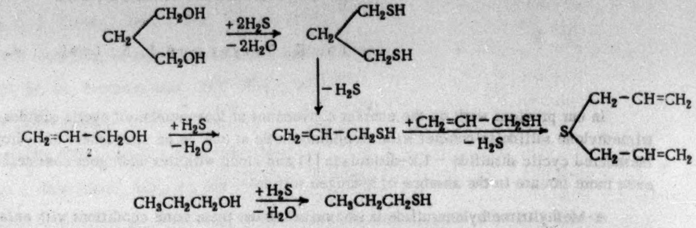


The decomposition of trimethylene oxide was quite considerable and was even more intensified by passage over aluminum oxide in a stream of hydrogen sulfide. Propionaldehyde, acrolein, propyl and allyl alcohols and also a mixture of propyl and allylmercaptans were again detected in the products of this latter reaction.

In the present work, joint dehydration of trimethyleneglycol and hydrogen sulfide in the presence of aluminum oxide was also conducted. A mixture of propionaldehyde and acrolein, propyl and allyl mercaptans, and also propyl and allyl alcohols, ditrimethyleneglycol, diallylsulfide and trimethylenedithiol was contained in the reaction products.

The formation of the sulfur compounds indicated above can be represented by the following reactions: the formation of trimethylenedithiol as a result of the joint dehydration of trimethyleneglycol and hydrogen sulfide;

the formation of allyl-mercaptan as a result of the cleavage of the hydrogen sulfide molecule from trimethylenedithiol or of the joint dehydration of allyl alcohol (obtained both from the oxide and from the diol) and hydrogen sulfide; the formation of diallylsulfide as a result of the cleavage of a molecule of hydrogen sulfide or two molecules of allylmercaptan; the formation of propylmercaptan as a result of the joint dehydration of propyl alcohol (obtained both from the oxide and from the diol) and of hydrogen sulfide.


$CH_2(CH_2OH)_2 \xrightarrow[-2H_2O]{+2H_2S} CH_2(CH_2SH)_2$
$-H_2S$
$CH_2{=}CH-CH_2OH \xrightarrow[-H_2O]{+H_2S} CH_2{=}CH-CH_2SH \xrightarrow[-H_2S]{+CH_2{=}CH-CH_2SH} S(CH_2-CH{=}CH_2)_2$
$CH_3CH_2CH_2OH \xrightarrow[-H_2O]{+H_2S} CH_3CH_2CH_2SH$

Thus, neither trimethylene oxide nor trimethyleneglycol is converted during its passage over aluminum oxide in a stream of hydrogen sulfide into trimethylenesulfide or into heterocyclic compounds with a different number of hetero-atoms and bonds in the ring. This strikingly differentiates the β-oxides and the β-glycols, both from the γ-oxides and γ-glycols which under such conditions smoothly form tetramethylenesulfide [6], and from the α-oxides and α-glycols, which, although incapable of being converted into a three-membered sulfur containing heterocyclic ring, form six-membered saturated heterocyclic rings with two distinct or identical hetero-atoms in the 1,4 position [7] or – at higher temperatures – a five membered heterocyclic aromatic ring – thiophene [8].

EXPERIMENTAL

I. Behavior of Trimethylene Oxide during Contact with Aluminum Oxide

Trimethylene oxide – m.p. 45.7-46.5° (741 mm); n_D^{20} 1.3915; d_4^{20} 0.9001 (literature data: m.p. 45.5-47.5°; n_D^{25} 1.3895; d_4^{25} 0.8930 [9]) – was passed rapidly over the catalyst distributed as a 35 cm layer in a tube in a weak stream of nitrogen at a rate of 7-8 g/hour.

250°. 20 g of catalyzate was obtained from 47 g of trimethylene oxide (15-16 g of oxide was introduced in each experiment). The lower (aqueous) layer of catalyzate (6 g) was saturated with magnesium sulfate. The small layer of oil (about 1 g) which then separated was added to the oily layer of the catalyzate which was then dried with anhydrous magnesium sulfate. Distillation of the aqueous layer of the catalyzate (b.p. 99° at 752 mm) demonstrated that it contained no higher-boiling residue.

The oily layer of catalyzate was distilled from a flask with a high, narrow fractionating column; 2.2 g of a fraction with a b.p. of 45-58° (758 mm), n_D^{20} 1.3770, and 1.2 g of a fraction with a b.p. of 93-97°, n_D^{20} 1.3919, and also 2.6 g of an intermediate fraction and 6 g of a resinous residue were obtained.

1. Composition of the Fraction with a B.p. of 45-58°. The Raman spectrum of the fraction with a b.p. of 45-58° showed that it contained acrolein and propionaldehyde and did not contain trimethylene oxide [presence in the spectrum of the frequencies 340 (0.8), 570 (1.5), 1162 (1.2), 1282 (15), 1364 (4), 1700 (40) cm^{-1}, and also of the frequencies 516 (2), 850 (52), 1392 (0.5), 1457 (10), 1732 (0.8) cm^{-1}, respectively characteristic of acrolein and propionaldehyde, and the absence of the frequencies 1028, 1178, 1453, 1495 cm^{-1}, characteristic of trimethylene oxide].*

We utilized the capacity of acrolein to polymerize with formation of disacryl upon prolonged heating to separate the aldehydes.

Acrolein. 1.8 g of the fraction was heated 9 hours with a reflux condenser. After distilling off the propionaldehyde, disacryl (0.4 g) remained – a transparent mass, melting around 85° and evolving acrolein on prolonged heating.

Propionaldehyde (1.2 g) distilled off from the disacryl, had the following constants: b.p. 47-49° (750 mm); n_D^{20} 1.3645; d_4^{20} 0.8072; its 2,4-dinitrophenylhydrazone melted at 154-155°. No melting point depression was observed in a mixture of a sample with known 2,4-dinitrophenylhydrazone of propionaldehyde.

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* We express our deep appreciation to Prof. V. M. Tatevsky for his assistance in and valuable advice relative to the study of the Raman spectra.

The literature data for propionaldehyde: b.p. 47-48° (746 mm); n_D^{20} 1.3636; d_4^{20} 0.8066 [10]; for the 2,4-dinitrophenylhydrazone: b.p. 154.5-155° [11].

The fraction with a b.p. of 45-58° thus contained ~34% acrolein and ~66% propionaldehyde.

2. Composition of the Fraction with a B.p. of 93-97°. This fraction gave a positive reaction for the hydroxyl group and unsaturated bonds and, to judge by its constants, contained a mixture of allyl and propyl alcohols. Quantitative determination of the composition of this fraction was based on the catalytic hydrogenation of allyl alcohol in propyl alcohol which, as is known from the work of S. V. Lebedev [12], proceeds quantitatively in the presence of platinum black.

Hydrogenation of Allyl Alcohol. 1 g of the fraction under investigation in 10 ml of absolute ether was hydrogenated in the cold in the presence of 0.3 g of platinum black: 231 ml of hydrogen (N.T.P) was absorbed, which corresponded to a 60% content of allyl alcohol in the mixture. 0.9 g of propyl alcohol was obtained by distillation of the hydrogenation product: b.p. 96-97° (758 mm); n_D^{20} 1.3850; d_4^{20} 0.8039; melting point of the phenylurethane 50.5°. No melting point depression was observed in a mixture of a sample with known phenylurethane of propyl alcohol.

Literature data for propyl alcohol: b.p. 97-97.2° (752 mm); n_D^{20} 1.3854; d_4^{20} 0.8041 [10]; for the phenylurethane of propyl alcohol: m.p. 50° [13].

350°. During the passage of 15.7 g of trimethylene oxide over aluminum oxide decomposition proceeded so strongly that only 3.4 g of catalyzate (of which 2 g was water) was obtained; it was not investigated in greater detail.

II. Behavior of Trimethylene Oxide during Contact with Aluminum Oxide in a Stream of Hydrogen Sulfide

250°. Trimethylene oxide was passed over aluminum oxide at a rate of 7-8 g/hour in a stream of hydrogen sulfide, admitted at a rate of 10-12 liters/hour (molar ratio of trimethylene oxide:hydrogen sulfide = 1:3). From 82 g of trimethylene oxide (13-14 g was taken for each experiment) 38 g of catalyzate was obtained. The aqueous layer (20 g) was saturated with magnesium sulfate, and the oily layer (~1 g) which separated was added to the oily reaction product (18 g). Subsequent distillation of the aqueous layer indicated that it contained no organic compounds.

The reaction product, dried with anhydrous magnesium sulfate, was distilled from a flask with a high narrow fraction column: 1.3 g of a fraction with a b.p. 47-55°, 1.5 g of a fraction with a b.p. of 55-80°, 0.1 g of a fraction with a b.p. of 80-93°, 4.5 g of a fraction with a b.p. of 93-97°, 1 g of a fraction with a b.p. of 97-150° and 8 g of a resinous residue were isolated.

The fraction with a b.p. of 47-55° (n_D^{20} 1.3805), as was described in the case of the passage of trimethylene oxide over aluminum oxide in the absence of hydrogen sulfide, was a mixture of propionaldehyde and acrolein (positive silver mirror formation reaction, positive reaction for double bonds). The 2,4-dinitrophenylhydrazone, obtained for this fraction melted at 140-145°, that is, it consisted of a mixture of the hydrazones of propionaldehyde and acrolein.

The fraction with a b.p. of 55-80° (n_D^{20} 1.4210) gave a positive qualitative reaction for the sulfhydryl group. An ether was obtained by the action of 2,4-dinitrochlorobenzene on an alkaline solution of this fraction which melted at 68° (the melting point of the allyl ether of 2,4-dinitrothiophenol is 72°; the m.p. of the propyl ether 81°).

5.230, 5.630 mg sub.: 2.085, 2.250 mg $SO_4^{=}$. Found %: S 13.31, 13.34. $C_9H_8O_4N_2S$. Calculated %: S 13.35.

According to the analytical data and the melting point, the ether obtained consisted of an allylmercaptan derivative in which an admixture of the corresponding propylmercaptan derivative caused the melting point depression.

The Raman spectrum of the fraction with a b.p. of 93-97° (n_D^{20} 1.3963), showed it to be primarily composed of propyl alcohol [presence in the spectrum of the frequencies 859 (12), 886 (3), 968 (2), 1050 (0.3), 1296 (6), 1457 (10) cm^{-1}] and that it also contained a small quantity of allyl alcohol [presence in the spectrum of the frequencies 908 (0.4), 992 (0.4), 1640 (8) cm^{-1}]; these frequencies were much less intense than the propyl alcohol frequencies. Trimethylene sulfide was completely absent from this fraction, inasmuch as the frequencies characteristic of the C−S bond (in the region of 650-700 cm^{-1}), and also the frequencies characteristic of trimethylene sulfide (671, 938, 970, 1439 cm^{-1}), were absent from the spectrum. Separation of propyl alcohol from the allyl alcohol was accomplished by the action of bromine on an ethereal solution of the fraction at minus 40-45° (until the appearance of a weak color that did not disappear).

0.5 g of bromine was consumed in the bromination of 2 g of this fraction, which corresponded with a content of 0.5 g of allyl alcohol. During distillation of the reaction products 1.5 g of propyl alcohol was distilled off: b.p. 96-97.5° (748 mm); n_D^{20} 1.3840; d_4^{20} 0.8025; m.p. of the phenylurethane 50°.

III. Joint Dehydration of Trimethyleneglycol and Hydrogen Sulfide in the Presence of Aluminum Oxide

Trimethyleneglycol – b.p. 109-110° (12 mm); n_D^{20} 1.4390; d_4^{20} 1.0570; literature data: b.p. 109-110° (12 mm); n_D^{20} 1.4398; d_4^{20} 1.0597 [14]; m.p. of the bis-phenylurethane 137-137.5° [15]– was passed over aluminum oxide at a rate of 10 g/hour in a stream of hydrogen sulfide (rate of introduction of the hydrogen sulfide 10-12 liters/hour); molar ratio of glycol:hydrogen sulfide = 1:4.

250°. 193 g of catalyzate was obtained from 254 g of trimethyleneglycol (24-25 g of glycol was taken for each experiment). By distillation of the aqueous layer of the catalyzate (132 g) a low boiling distillate (below 99°), water, and a high boiling portion which was further vacuum distilled, were isolated. After drying with anhydrous magnesium sulfate the low boiling distillate was redistilled from a flask with a high narrow fractionating column and yielded 0.2 g of a fraction with a b.p. ranging up to 78°; 5 g of a fraction with a b.p. of 78-93°; n_D^{20} 1.3871; and 4 g of a fraction with a b.p. of 93-97°, n_D^{20} 1.3950. The Raman spectra of these two fractions indicated the closeness of their composition, the presence in them of a mixture of allyl and propyl alcohols [presence in the spectra of the frequencies respectively of 859/860 (30), 888 (30), 1057 (1), 1106 (1), 1454/57 (10) cm^{-1} and 1293 (15) and 1648 (50) cm^{-1}] and the absence of compounds with a sulfide group (in particular, the absence of trimethylenesulfide). These fractions were combined with each other and subsequently with a fraction with an analogous composition (this was also established by the Raman spectrum) with a b.p. of 95-98° which was separated from the oily layer of the catalyzate (see below).

The following substances were isolated from the aqueous layer of the catalyzate by vacuum distillation:

a) unchanged trimethyleneglycol – 11.7 g; b.p. 110-112° (13 mm); n_D^{20} 1.4385; d_4^{20} 1.0560; m.p. of the bisphenylurethane 137-138°, no melting point depression was observed in a mixture of a sample with known bisphenylurethane of trimethyleneglycol;

b) ditrimethyleneglycol – 1.9 g; b.p. 152-155° (13 mm); n_D^{20} 1.4520; d_4^{20} 1.0553; m.p. of the phenylurethane 97.5-98°; no melting point depression was observed in a mixture of a sample with known phenylurethane of ditrimethyleneglycol.

Literature data for ditrimethyleneglycol: b.p. 155-160° (15 mm); d_{17}^{17} 1.064; for the phenylurethane m.p. 104-105° [16].

The distillate which passed over below 180° was removed from the oily layer of the catalyzate (dried with anhydrous magnesium sulfate) by distillation from a Favorsky flask. The following were separated by subsequent distillation in a column with an efficiency of 18 theoretical plates: 2.6 g of a fraction with a b.p. of 50-76° (765 mm), n_D^{20} 1.4410; 1.8 g of a fraction with a b.p. of 76-95°; 5.4 g of a fraction with a b.p. of 95-98°, n_D^{20} 1.3994; 1.6 g of a fraction with a b.p. of 98-132°, n_D^{20} 1.4193; 1.6 g of a fraction with a b.p. of 132-145°, n_D^{20} 1.4519; 3.8 g of a fraction with a b.p. of 145-165°, n_D^{20} 1.4780; 1.4 g of a fraction with a b.p. of 165-174.5°, n_D^{20} 1.5340, and 10 g of residue.

The fraction with a b.p. of 50-76°, to judge by its reactions, contained aldehyde and mercaptan, which could not be successfully isolated from the small quantity of the fraction. The 2,4-dinitrophenylhydrazone obtained from this fraction melted at 135-138° (the 2,4-dinitrophenylhydrazone of propionaldehyde melts at 154-155°, acrolein at 165°). There is no doubt that propionaldehyde and acrolein were present in this fraction, inasmuch as a mixture of them was formed by the dehydration of trimethyleneglycol over aluminum oxide [4]. The presence of mercaptans in this fraction was demonstrated by the formation of lead salts.

The fraction with a b.p. of 95-98° was combined with the corresponding fractions (with b.p. of 78-93 and 93-97°), isolated from the aqueous layer of the catalyzate. Separation of the allyl and propyl alcohols contained in this combined fraction was carried out in the following manner:

Allyl alcohol. Bromine was added in drops until a faint color that did not disappear was obtained, to 5 g of the fraction in 10 ml of ether at minus 40-45°. After unchanged propyl alcohol had been distilled off, a dibromopropyl alcohol was obtained (6.5 g) with a b.p. of 104-105° (15 mm); n_D^{20} 1.5554; d_4^{20} 2.0858; phenylurethane m.p. 82-83°; no melting point depression was observed in a mixture of a sample with known phenylurethane of dibromopropyl alcohol.

Literature data for dibromopropyl alcohol: b.p. 111-114° (20 mm); d_4^{25} 2.1197 [17]; n_D^{20} 1.5577 [18]; for the phenylurethane m.p. 83-84° [19].

Propyl alcohol (3.2 g), distilled off from the fraction under investigation, had a b.p. of 95.5-97° (760 mm); n_D^{20} 1.3845; d_4^{20} 0.8030 after bromination; the phenylurethane m.p. 50°; no melting point depression was observed in a mixture of a sample with known phenylurethane of propyl alcohol.

14.4 g of a mixture of allyl and propyl alcohols which contained 64% of propyl and 36% of allyl alcohol was isolated from the catalyzate in this manner.

Trimethylendithiol. The fraction with a b.p. of 165-174.5° almost completely distilled over at 168-169° (765 mm), had a n_D^{20} 1.5340; d_4^{20} 1.0854; gave a positive reaction for the sulfhydryl group and consisted of trimethylenedithiol; m.p. of the dibenzoate 55.5-56.5°; no melting point depression was observed in a mixture of a sample with a known sample of the dibenzoate.

Literature data for trimethylenedithiol: b.p. 169-170° [20]; n_D^{25} 1.5371; d_4^{25} 1.0775 [21]; m.p. of the dibenzoate 55.5-56.3° [22].

350°. From 244 g of trimethyleneglycol passed over aluminum oxide in a stream of hydrogen sulfide (24-25 g of glycol were taken for each experiment). 142 g of catalyzate was obtained.

4 g of a low boiling distillate with a b.p. of 50-99° was distilled off from the aqueous layer of the catalyzate (90 g). The residue consisted of water and contained no high boiling substances. The low boiling distillate was added to the oily layer of the catalyzate (52 g), from which a distillate passing over below 180° was obtained after drying with anhydrous magnesium sulfate by distillation from a Favorsky flask. The distillate was subsequently fractionated in a column with an efficiency of up to 18 theoretical plates; 2.2 g of a fraction with a b.p. of 46-87° (759 mm); 0.6 g of a fraction with a b.p. of 87-99°; 3.2 g of a fraction with a b.p. of 100-138°; 3 g of a fraction with a b.p. of 138-144°; 3.8 g of a fraction with a b.p. of 144-174°; and also a considerable residue (30 g) consisting of polymerization product and resin were isolated.

The fraction with a b.p. of 46-87° (n_D^{20} 1.4107; d_4^{20} 0.8360) gave a positive reaction for aldehyde and sulfohydryl groups. The 2,4-dinitrophenylhydrazone melted at 133-136° and evidently consisted of a mixture of the hydrazones of propionaldehyde and acrolein. The 2,4-dinitrochlorobenzene ether was formed from the fraction of the 2,4-dinitrothiophenol with a m.p. of 57-59°. The depression of the melting point of the 2,4-dinitrothiophenol ether which was observed is due, as was indicated above, to the presence in it of a mixture of the allyl and propyl ethers of 2,4-dinitrothiophenol.

The fraction with a b.p. of 87-99° (n_D^{20} 1.4320) gave a positive reaction for the alcohol group and unsaturated bonds, but was not investigated in more detail. The fraction with a b.p. of 100-138° (n_D^{20} 1.4460) gave a positive reaction for the sulfide group; no cyclic sulfides were detected in it.

Diallylsulfide. The fraction with a b.p. of 138-144° had a n_D^{20} 1.4879, d_4^{20} 0.9050, exhibited a positive reaction for the sulfide group and consisted of diallylsulfide. Its molecular compound with silver nitrate melted at 151-151.5°.

Literature data for the diallylsulfide: b.p. 138-140°; n_D^{20} 1.4895 [23]; $d_4^{26.8}$ 0.8876 [24]; for $2C_3H_5)_2S \cdot AgNO_3$ m.p. 152° [25].

Trimethylenedithiol. The fraction with a b.p. of 144-174° was primarily composed of trimethylenedithiol (about 75%). 0.9 g of 1,2-dithiolane* which melted at 76-77° was isolated from 1.5 g of the fraction in ethereal solution by oxidizing it with atmospheric oxygen; no melting point depression was observed in a mixture of a sample with a known sample of 1,2-dithiolane.

Literature data: m.p. of 1,2-dithiolane 76.5-77.5° [1].

SUMMARY

1. Trimethylene oxide during passage over aluminum oxide at 250° gives the very same reaction products that are obtained from trimethylene glycol under the same conditions: propionaldehyde, acrolein, propyl and allyl alcohols. Along with this a very strong decomposition of trimethylene oxide occurs.

2. Trimethylene oxide and trimethyleneglycol during passage over aluminum oxide in a stream of hydrogen sulfide also form identical reaction products: a mixture of propionaldehyde and acrolein, a mixture of propyl- and allylmercaptans, propyl and allyl alcohols. From trimethyleneglycol, diallylsulfide and trimethylenedithiol are formed in addition. Decomposition of trimethylene oxide in an atmosphere of hydrogen sulfide was even more intense.

3. Neither trimethylene oxide nor trimethyleneglycol is converted by passage over aluminum oxide in a stream of hydrogen sulfide into trimethylene sulfide or other heterocyclic compounds with other hetero-atoms or a different number of bonds in the ring.

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* It was established in independent experiments that 1,2-dithiolane is obtained in almost quantitative yield by the oxidation of an ethereal solution of trimethylenedithiol with atmospheric oxygen.

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* See Consultants Bureau Translation, page 2243.

** See Consultants Bureau Translation, page 885.

XLIII. THE CONVERSION OF α-ACETOFURAN, FURFURAL AND FURYLIDENEANILINE INTO N-PHENYLPYRROLE

Yu. K. Yuryev and E. G. Vendelshtein

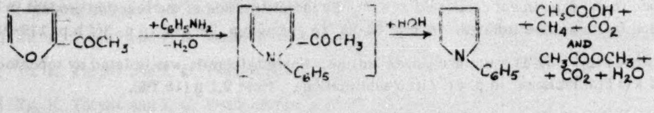
The catalytic conversion of oxygen-containing heterocyclic compounds into rings with other hetero-atoms –nitrogen, sulfur, selenium– pioneered by one of us, was studied in a large number of compounds of the furan, furanidine (tetrahydrofuran), Δ^2-dihydropyran and tetrahydropyran [1] series, including those compounds containing such functional groups as the hydroxymethyl, mercaptomethyl and carbalkoxy groups in the α-position of the ring.

We studied the catalytic conversions of the furyl and tetrahydrofuryl alcohols [2, 3], tetrahydrofurfurylmercaptan [3], and also of the methyl ethers of pyromucic [4] and tetrahydropyromucic acids [5], and established that these functional derivatives of furan and furanidine act in various ways depending on the nature of the functional groups. Thus, furyl alcohol with ammonia gave a mixture of high-boiling condensation products and is completely decomposed and resinified by the action of hydrogen sulfide. Tetrahydrofuryl alcohol and tetrahydrofurfurylmercaptan with ammonia or hydrogen sulfide initially undergo the usual isomerization with enlargement of the ring and formation of Δ^2-dihydropyran, which at once gives a mixture of pyridine and piperidine [2], or, respectively Δ^2-dihydrothiopyran As regards the methyl esters of pyromucic and tetrahydropyromucic acids, during their reaction with aniline, cleavage of the carbomethoxy groups proceeds with substitution at the hydrogen and formation of N-phenylpyrrole [4] and, respectively, N-phenylpyrrolidine [5].

It has been shown in the present work that during the reaction of α-acetofuran with aniline in the presence of aluminum oxide at temperatures of 400, 420, 450 and 475°, N-phenylpyrrole is obtained in place of the expected N-phenyl-α-acetopyrrole. At 400° the yield of N-phenylpyrrole reached 29%, i.e., was higher than that obtained during the conversion of furan by the action of aniline at 465° (24%) [6], but lower than during the preparation of pyromucic acid at 400° from the methyl ester (35%) [4].

The better yield of N-phenylpyrrole during its preparation from more complex substances and at milder temperature conditions serves as a striking illustration of the weakening of the strength of the oxygen bridge bond of the furan ring under the influence of carbonyl and carbalkoxy groups linked to the α-carbon atom of the ring.

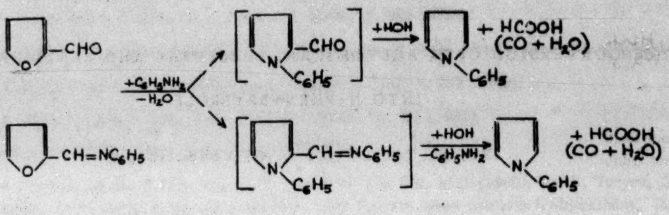
Substitution of the acyl group for hydrogen when N-phenyl-α-acetopyrrole (and also α-acetofuran) is being formed, could proceed only during the hydrolytic cleavage of the ketone. Inasmuch as carbon dioxide and methane are contained in the gaseous reaction products, and acetone in the light fraction of the catalyzate – all these are products of the decomposition and ketonization of the decomposition and ketonization of acetic acid– the mechanism of the formation of N-phenylpyrrole from α-acetofuran and aniline may be represented by the following scheme



It was shown in a separate experiment that at 475° acetic acid decomposes on contact with aluminum oxide, yielding chiefly carbon dioxide and methane and also a small quantity of acetone.

The reaction of furfural and also of furfurylidenaniline with aniline under these conditions also leads to the formation of N-phenylpyrrole and high-boiling condensation products. The course of these reactions is evidently analogous to the preceding (see scheme at top of following page).

Thus, α-acetofuran, furfural, furfurylidenaniline and the methyl esters of pyromucic and tetrahydropyromucic acids undergo not only replacement of the oxygen bridge by the phenylimino group, which, in our opinion, is the first of a series of reactions constituting a complex process of catalytic conversion of these compounds, but also undergo substitution of the functional groups by hydrogen.



Consequently, if a carbonyl, carbalkoxy or azomethine group is bound to an α-carbon atom of the furan or furanidine ring, under the conditions of the catalytic conversion reaction of heterocyclic compounds, such a substitutent is split off and replaced with a hydrogen atom.

EXPERIMENTAL

N-Phenylpyrrole from α-Acetofuran and Aniline

400°. A mixture of 15 g of α-acetofuran (b.p. 173-174° at 757 mm; m.p. 28°) and 22 g of freshly prepared aniline (molar ratio 1:2) was passed over aluminum oxide at a rate of 5-6 drops per minutes in a stream of nitrogen. The reaction product (26 g) was separated from water, dried with fused sodium hydroxide and redistilled in a vacuum at 2 mm; the following fractions were isolated: 1st b.p. 50-65°, 11 g; 2nd b.p. 65-75°, 8 g; 3rd b.p. 75-110°, 5 g; the residue in the flask resinified.

The first fraction had a n_D^{20} 1.5848 and consisted of unchanged aniline. From the second and third fractions after repeated distillation there were isolated a fraction with a b.p. of 78-92° (2 mm) and a solid substance with a m.p. of 57° which gave an intense pyrrole reaction on pine shaving (pine wood test) and was resinified by concentrated hydrochloric acid. After distillation, the substance melted at 61° and consisted of N-phenylpyrrole. A mixture of a sample with a known sample of N-phenylpyrrole exhibited no melting point depression. Yield 3.5 g (29%).

Mild distillation from the aqueous layer of the catalyzate established the presence of an insignificant quantity of acetone (formation of iodoform).

Literature data for N-phenylpyrrole: m.p. 61° [6].

420°. A mixture of 18 g of α-acetofuran and 27 g of aniline gave 36 g of catalyzate which was extracted with ether. After distilling of the ether from the extract which was dried with fused sodium hydroxide, the reaction product was vacuum distilled at 3 mm and the following fractions were isolated: 1st b.p. 55-65°, 18 g; 2nd b.p. 65-75°, 6.5 g; 3rd b.p. 75-110°, 7 g.

The first fraction (n_D^{20} 1.5853) – was unchanged aniline. By repeated distillation of the second and third fractions N-phenylpyrrole was isolated: m.p. 61° (after sublimation). Yield 3.8 g (16%).

450°. The mixture of 15 g of α-acetofuran and 22 g of aniline (1:2) gave 25.5 g of catalyzate which was treated as described in the experiment conducted at 420°. By the distillation of the reaction product in a vacuum at 7 mm the following fractions were isolated: 1st b.p. 85-95, 14 g; 2nd b.p. 95-110°, 5 g; 3rd b.p. 110-135°, 5 g.

The first fraction (n_D^{20} 1.5861) – was unchanged aniline. N-phenylpyrrole was isolated by repeated distillation from the 2nd and 3rd fractions: m.p. 61° (after sublimation). Yield 2.1 g (10.7%).

475°. The following fractions were isolated by the vacuum distillation (at 2 mm) of the reaction product obtained from a mixture of 8 g of α-acetofuran and 14 g of aniline: 1st b.p. 50-55°, 9 g; 2nd b.p. 55-77°, 1.5 g; 3rd b.p. 77-78°, 1 g; 4th b.p. 78-95°, 0.5 g.

Unchanged aniline was contained in the first and second fractions; the 3rd fraction (m.p. 57.5°) consisted of N-phenylpyrrole, which after sublimation melted at 61°. Yield: 1 g (10%).

Decomposition of acetic acid. 105 g of glacial acetic acid was passed over aluminum oxide at 475-480°. 42 g of condensate was obtained; 20.1 liter (N.T.P.) was collected. 6 g of acetone was isolated from the condensate: b.p. 56°. The composition of the gas: CO_2 47.9%, unsaturated hydrocarbons 19.95%, O_2 3.09%, CO 0.58%, H_2 3.69%, methane + other saturated hydrocarbons 13.21%; residue 11.58%.

Results of the Analysis of the Gases Formed during the Conversion of α-Acetofuran into N-Phenylpyrrole

Temperature of the experiment (in °)	Quantity of gas (N.T.P.) (in liters)	Composition of the gas (in %)					
		CO_2	Unsaturated hydrocarbons	O_2	CO	Methane and other fuel gases	N_2
400	2.750	1.6	0.0	8.1	0.2	2.4	87.7
420	3.420	8.0	3.6	3.3	8.6	8.5	68.0
475	4.280	4.7	2.5	4.3	5.1	12.2	70.2

N-Phenylpyrrole from Furfural and Aniline

Furfural and aniline (100 g of furfural and 200 g of aniline) were introduced into a reaction tube in such a manner that their reaction could proceed only in a zone filled with aluminum oxide. The reaction was conducted at 450°. The catalyzate obtained (188 g) was extracted with ether and dried with roasted potash. After the ether had been driven off, the following fractions were isolated by vacuum distillation of the residue at 8 mm: 1st b.p. 76-78°, 151 g; 2nd b.p. 78-95°, 0.8 g; 3rd b.p. 95-102°, 6.5 g; 4th b.p. 102-110°, 5 g; 5th b.p. 110-160°, 5 g; residue (17 g) – resin.

The 1st fraction (n_D^{20} 1.5842) was unchanged aniline. 5.6 g of N-phenylpyrrole which melted at 61° after sublimation, was isolated from the 3rd fraction which crystallized on cooling. A mixed melting point test with known N-phenylpyrrole displayed no depression. The yield was 3.8% of the theoretical.

N-Phenylpyrrole from Furfurylidenaniline and Aniline

A mixture of 200 g of furfurylidenaniline (b.p. 161-162° at 19 mm; m.p. 56-57°) and 225 g of aniline (1:2) were passed over aluminum oxide at 450° at a rate of 7-8 drops per minute in a stream of nitrogen. The catalyzate (295 g) was extracted with ether and dried with sodium hydroxide. After the ether had been driven off, the residue was redistilled in a vacuum. 8.5 g of a crystalline substance which consisted of N-phenylpyrrole and melted after sublimation at 61°, was isolated. A sample in a mixture with known N-phenylpyrrole displayed no melting point depression The yield was 5% of the theoretical.

SUMMARY

1. The reaction of α-acetofuran, furfural and also of furfurylidenaniline with aniline in the presence of aluminum oxide at 400-475° leads to the formation of N-phenylpyrrole.

2. The carbonyl and azomethine groups bond to the α-carbon atom to the furan or furanidine ring, similarly to the carbalkoxy group, are split off by the catalytic conversion of these functional derivatives of the furan and furanidine series into rings with other hetero-atoms, and are replaced by a hydrogen atom.

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* See Consultants Bureau Translation, page 751.

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*** See Consultants Bureau Translation, page 287.

INVESTIGATION OF ALKALOIDS OF SPECIES OF STERNBERGIA

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The present work on the investigation of alkaloids of species of Sternbergia is a continuation of work begun by us on the study of the alkaloids of the Amaryllis family [1].

The flora of Azerbaidzhan has been studied comparatively little up to now with reference to its alkaloid content. The plants examined constitute only an insignificant part of the 4000 species of plants which grow in the territory of the Azerbaidzhan SSR.

We investigated alkaloids of two species of the Amaryllidaceae for the first time: Sternbergia fischeriana and Sternbergia lutea which are representatives of the wild flora of Azerbaidzhan.

Sternbergia fischeriana was collected in the Karyaginsk region after the flowering phase (1950), Sternbergia lutea —in the Baku botanical garden at the time of and after flowering (1949). The fact that these species contain alkaloids was established for the first time by R. Ya. Rzazade.

The alkaloids of St. f. and St. l. were isolated in the usual way by dichloroethane extraction with subsequent treatment of the dichloroethane extract with sulfuric acid. The chief constituent part of the total alkaloids of both plants was extracted at once by the alkalinization of the sulfuric acid solution. It consisted of an individual crystalline alkaloid, identified by its properties as well as by the constants of its salts, as the previously well-known lycorine.

From St. f., aside from lycorine, we isolated two alkaloids, the separation of which was accomplished by means of their differing solubility in water.

One of them, named sternine, has the composition $C_{18}H_{21}O_3N$, m.p. 231-232°, $[\alpha]_D$ + 12.5° and gives a series of crystalline salts. Although sternine appeared to be a monoacidic tertiary base, the presence in it of the methylimide group was not detected. Of the three oxygen atoms present in the sternine molecule, two are found in the form of methylenedihydroxy groups and one in the form of a hydroxyl group of a non-phenolic character. The expanded formula of sternine can be expressed in the following fashion: $C_{17}H_{18}N(OH)(CH_2O_2)$.

The second alkaloid isolated by us from St. f. and denoted by us base (III), had a m.p. of 212-213°, was optically inactive and gave a series of crystalline salts. Because of its small quantity, we did not succeed in investigating it in greater detail.

From the second plant examined by us —St. l.— a new alkaloid called luteine was isolated along with lycorine. The poor solubility of luteine in acetone was utilized to isolate it from the total alkaloids and to purify it.

Luteine has the composition of $C_{17}H_{19}O_5N$, $[\alpha]_D$ −18.4°, m.p. 185-186°, and gives a series of crystalline salts. The nitrogen of luteine has a tertiary character. Two oxygen atoms are found in the form of hydroxyl groups, one atom in the form of a methoxyl group and two in the form of a methylenedihydroxy group. The expanded formula of luteine can be expressed as $C_{15}H_{12}N(OH)_2(OCH_3)(CH_2O_2)$.

The occurrence in the plant of sternine and luteine together with lycorine, and also their close absorption spectra in the ultraviolet region permits one to assume that both new alkaloids have a phenanthridine nucleus.

EXPERIMENTAL

Extraction of the Alkaloids from the Bulbs of Sternbergia fischeriana

71 kg of dried and crushed bulbs of St. f. were moistened with 10% ammonia and extracted with dichloroethane. The dichloroethane extract was treated with 10% sulfuric acid. During the alkalinization of the sulfuric acid solution with ammonia, a finely crystalline, grayish precipitate separated out which was filtered off and washed with water. The yield of crystalline base was 152 g (0.21% of the weight of the dry bulbs).

The ammoniacal mother liquor was saturated with potash and treated with chloroform. After the chloroform had been evaporated off and the solution reduced to small volume, a resinous precipitate, which was separated from the chloroform mother liquor, separated out. 33 g of a resinous precipitate was obtained.

After the chloroform had been completely distilled off from the mother liquor, a residue (52 g) was collected in the form of a viscous resinous mass.

The total alkaloids obtained amounted to 237 g in all or 0.33% of the weight of the dry bulbs.

Purification of the crystalline base. 152 g of the crystalline base was repeatedly boiled down with acetone. The residue (144 g) with a m.p. of 247-248° was treated with hydrobromic acid. The crystalline hydrobromide obtained was washed with acetone. After crystallizing it three times from water, 126 g of a colorless crystalline hydrobromide with a m.p. of 209-210° and $[\alpha]_D$ +37.3° was obtained. A sample of the hydrobromide mixed with lycorine hydrobromide did not exhibit any melting point depression.

Precipitation with ammonia produced 42 g of a colorless finely crystalline base with a m.p. of 264-265° from 50 g of the hydrobromide with a m.p. of 209-210°. A mixed sample with lycorine gave no lowering of the melting point.

Purification of the resinous precipitate precipitated from the chloroform extract. Isolation of sternine hydrobromide. The resinous residue (30 g) was dissolved in 5% sulfuric acid, the acidic solution was separated from the insoluble resin, and the base was fractionally precipitated with sodium bicarbonate with subsequent ether extraction. 4 fractions were obtained.

From the 1st fraction, a dark brown resinous base which was not successfully purified was isolated.

From the 2nd fraction, 2.8 g of a yellow, viscous base was isolated, which crystallized after trituration with alcohol. After washing with alcohol, 2.45 g of almost colorless, crystalline, sternine, with a m.p. of 216-218°, was obtained.

From the 3rd fraction, 1.9 g of the same base with a m.p. of 215-216° was isolated.

From the 4th fraction, lycorine (3.5 g) with a m.p. of 261-265° was isolated, from which was obtained the hydrobromide with a m.p. of 209-210°.

4.35 g of sternine with a m.p. of 216-218° was dissolved in 8 ml of water at 70-80°; the solution was filtered off from the water-insoluble admixture of lycorine (0.5 g).

After addition of hydrobromic acid to the aqueous solution, a crystalline precipitate of sternine hydrobromide separated out (3.2 g), and was washed with acetone and recrystallized from water with activated carbon. 2.8 g of colorless crystalline hydrobromide with a m.p. of 226-226.5° was obtained. The sternine hydrobromide was readily soluble in warm water, difficultly soluble (1:40) in cold, and almost insoluble in alcohol and in acetone.

3.497 mg sub.: 6.941 mg CO_2; 1.878 mg H_2O. 3.515 mg sub.: 7.000 mg CO_2; 1.810 mg H_2O. 9.645 mg sub.: 0.294 ml N_2 (21°, 749.5 mm). 7.810 mg sub.: 0.243 ml N_2 (21.5°, 744 mm). 3.107 mg sub.: 1.451 mg AgBr. 3.502 mg sub.: 1.672 mg AgBr. 0.1388 g sub.: 0.0062 g H_2O. Found %: C 54.13, 54.31; H 6.00, 5.76; N 3.59, 3.51; Br 19.87, 20.32; H_2O 4.46. $C_{18}H_{21}O_3N \cdot HBr \cdot H_2O$. Calculated %: C 54.27; H 6.03; N 3.51; Br 20.09; H_2O 4.52. 0.1834 g sub. in 15 ml water, l = 2 dm: α_D +0.58°; $[\alpha]_D$ + 23.7°.

Isolation of free sternine. 2.5 g of sternine hydrobromide with a m.p. of 226-226.5° was dissolved in warm water and precipitated with ammonia. The base precipitated in the form of a viscous resin and was dissolved in ether. After the ether had been evaporated off to small volume, crystalline base precipitated (1.5 g) with a m.p. of 231-232°. Sternine is quite soluble in chloroform and benzene, soluble with more difficulty in alcohol and water, and still more difficultly soluble in ether.

6.982 mg sub.: 0.50 ml CH_4 (20.5°, 740 mm); 7.711 mg sub.: 0.62 ml CH_4 (20°, 740 mm). Found %: OH 4.97, 5.58. $C_{18}H_{21}O_3N$. Calculated %: OH 5.68. 0.1018 g sub. in 15 ml alcohol, l = 2 dm: α_D +0.17°; $[\alpha]_D$ +12.5°.

Sternine hydrochloride with a m.p. 181-182° was obtained in the form of a colorless, finely crystalline precipitate by dissolving the base in aqueous hydrochloric acid.

Sternine picrate with a m.p. of 227-228° precipitated in the form of a yellow amorphous precipitate upon the addition of an aqueous solution of picric acid to an aqueous solution of the base.

Sternine chloroplatinate with a m.p. of 192-193° precipitated from the solution upon mixture of an aqueous solution of the base with platinic chloride.

Sternine iodomethylate. 0.2 ml of methyl iodide was added to a solution of 0.2 g of sternine in 4 ml of acetone. Upon heating on a water bath for 10-15 minutes, a colorless, crystalline precipitate of sternine iodomethylate with a m.p. of 202-203° separated out. After crystallization from alcohol its m.p. did not change.

Working up the chloroform mother liquor. Isolation of the base (III). 48 g of the resinous mass obtained after distilling off the chloroform with which the alkaloids of St. f were extracted, was dissolved in hydrochloric acid, and the solution separated from the resin which precipitated. The base was fractionally precipitated with sodium bicarbonate with subsequent chloroform extraction. 10 fractions were thus obtained.

The 1st fraction, a dark brown, resinous mass in appearance, was not subjected to investigation.

Fractions 2 through 10, consisting of a yellow, amorphous substance, were converted into the picrate. Since the picrates from fractions 2-4 did not have a clear melting point, they were not subjected to a more detailed investigation. The picrates from fractions 5 and 7 all had the same melting point of 217-219°.

From 3.7 g of the combined picrates of fractions 5-7, the base (III) was isolated, in the form of a yellow, viscous oil. It was dissolved in hydrobromic acid, from which the hydrobromide of base (III) crystallized; after washing with acetone and recrystallization from alcohol, the hydrobromide melted at 174-175°. The picrates of fractions 8-10, with m.p. 180-185°, were converted to the base with m.p. 260-265°, which gave no melting point depression in a mixture with lycorine.

Extraction of the Alkaloids of Sternbergia lutea

8 kg of dried and crushed bulbs of St. l. were moistened with 10% ammonia and extracted with dichloroethane. The dichloroethane extract was treated with 10% H_2SO_4. After alkalinization of the acidic solution with ammonia, a greyish crystalline base precipitated (4.6 g, 0.06% of the weight of the dry bulbs with a m.p. of 246-249°.

The ammonia solution was saturated with potash and treated with ether, and then with chloroform. From the ether was obtained 6.9 g of amorphous light yellow base, from the chloroform −3.5 g of a darker resinous base.

Isolation of lycorine. The greyish precipitate, which settled from the alkaline solution (4.6 g), was boiled with acetone. The base thus obtained with a m.p. of 256-257° was dissolved in hydrobromic acid. The crystalline hydrobromide which precipitated was washed with acetone and purified by crystallization from water with carbon. 3.15 g of hydrobromide with a m.p. of 209-210° was obtained. A mixed melting point sample with lycorine hydrobromide did not exhibit melting point depression. The base isolated from the hydrobromide had a m.p. of 264-265° and did not give a depression of the melting point in a mixed sample with lycorine.

Treatment of the ethereal extract. Isolation of luteine. Partial elimination of the ether with which the total alkaloids of St. l. had been extracted led to the separation of a crystalline precipitate of luteine (0.62 g) with a m.p. of 180-181°. From the ethereal mother liquor was isolated a resinous base (6.32 g) which was dissolved in hydrochloric acid; the solution was then separated from resin and saturated with sodium perchlorate. Luteine perchlorate precipitated in the form of a viscous mass which crystallized after trituration with water. 1.5 g of luteine perchlorate was obtained and had a m.p. of 122-123° after four-fold recrystallization from water. The free luteine with a m.p. of 180-181° was isolated from the perchlorate. Luteine which was recrystallized from acetone had a m.p. of 185-186°.

3.640 mg sub.: 8.542 mg CO_2; 2.004 mg H_2O. 3.681 mg sub.: 8.676 mg CO_2; 2.042 mg H_2O. 6.440 mg sub.: 0.265 ml N_2 (22°, 734 mm). 6.015 mg sub.: 0.251 ml N_2 (23°, 741 mm). 7.668 mg sub.: 6.90 ml 0.01 N $Na_2S_2O_3$. 9.48 mg sub.: 1.35 ml CH_4 (0°, 760 mm). 9.500 mg sub.: 1.31 ml CH_4 (0°, 760 mm). Found %: C 64.00, 64.21; H 6.16, 6.21; N 4.50, 4.68; OCH_3 9.30, 9.50; OH 10.88, 10.54. $C_{17}H_{19}O_5N$. Calculated %: C 64.35; H 6.00; N 4.59; OCH_3 10.18; 2OH 11.14. 0.9976 g sub. in 15 ml alcohol, $\underline{l}$ = 2 dm: $\alpha_D -0.24°$; $[\alpha]_D -18.4°$.

Luteine picrate was obtained with a m.p. of 190-192°, which after three-fold crystallization from alcohol had a m.p. of 201-202°. Luteine was quite soluble in water, alcohol, chloroform and benzene; more difficultly soluble in acetone and ether.

Methylation of luteine with methyl iodide. 0.1 g of luteine with a m.p. of 185-186° was dissolved in 5 ml of hot acetone, 0.2 ml of methyl iodide was added. After several minutes, a crystalline precipitate separated out, consisting of luteine iodomethylate (0.06 g) with a m.p. of 196-197°.

Treatment of the chloroform extract of the total alkaloids of Sternbergia lutea. 3.5 g of the viscous resinous base obtained from the chloroform extract of the total alkaloids was dissolved in hydrobromic acid; the solution was separated from the acid-insoluble reshol. Upon standing a crystalline precipitate of lycorine hydrobromide (0.4 g) with a m.p. of 209-210° (which did not give a melting point depression in a mixed sample with lycorine) separated out from the acidic solution. The mother liquor after the separation of the lycorine hydrobromide was alkalinized with ammonia and treated with ether. After driving off the ether to a small volume, a crystalline precipitate of luteine with a m.p. of 180-181° separated out.

SUMMARY

1. From Sternbergia fischeriana lycorine and two new alkaloids named sternine, with a composition of $C_{18}H_{21}O_3N$ and the base (III), were isolated. The expanded formula of sternine is: $C_{17}H_{18}N(OH)(CH_2O_2)$.

2. From Sternbergia lutea lycorine and a new alkaloid of the composition $C_{17}H_{19}O_5N$, named luteine, were isolated. The expanded formula of luteine is: $C_{13}H_9(NCH_3)(OH)_2(OCH_3)(CH_2O_2)$.

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ON THE STRENGTH OF CERTAIN BASES IN WATER AND ACETONE

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As was shown in preceding investigations, anabasine reacts with acids to form salts of varying composition [1, 2, 3]. However, the character of the reaction of anabasine with acids and the formation conditions of the salts depends to a significant extent on the nature of the solvent used; it is, therefore, of interest to determine the ionization constants of anabasine and certain other organic bases in various solvents.

To this end, we took as solvents water and acetone; the ionization constants in water of anabasine, N-methylanabasine, N-nitrosoanabasine and lupinine, and in acetone of anabasine, N-methylanabasine, lupinine, nicotine, trimethylamine and piperidine were determined.

The anabasine necessary for the work was isolated from technical anabasine sulfate by means of the copper anabasine salt. The purified anabasine boiled at 106-110° (4 mm) and had a n_D^{20} 1.5440.

Lupinine was isolated from the filtrate remaining after removal of the anabasine salt, and had a m.p. of 68-69° after recrystallization. N-Methylanabasine was obtained from purified anabasine [4] and had a b.p. of 99-100° (3 mm) and a n_D^{20} 1.5289. Nitrosoanabasine was obtained from the same anabasine, analogously to nitrosopiperidine [5]; its b.p. was 111-112° (6 mm). Chemically pure trimethylamine was used. Acetone after being carefully dried and redistilled in a column with 14 theoretical plates, had a b.p. of 55.5° (722 mm) and a n_D^{15} 1.3613.

All determinations were conducted at room temperature. The usual methods were employed for keeping water free of CO_2, and acetone free of moisture.

Determination of the ionization constants of the bases investigated in aqueous solutions was conducted by the usual spectrophotometric unbuffered method using the indicators thymol blue and tropeolin 000.

Piperidine with a b.p. of 104-105° (740 mm) and a n_D^{20} 1.5429, and isobutylamine with a n_D^{17} 1.3986 and a solution of chemically pure ammonia were taken as standard bases.

It is well-known that the methods of colorimetric determination of the ionization constants of acids and bases that are usually applied can be utilized only when the transition constants of the indicators in the given solvent are known, or when the comparative strength of the acid or base is known [14].

There is another method, proposed by V. I. Dulova and N. V. Vostrilova [6], in accordance with which determination of the transition constants of the indicators and of the ionization constants of acids and bases does not require knowledge of one of these quantities. Extending this method to aqueous solutions of bases, we determined the transition constants of the indicators alizarin yellow and alizarin red of $1.42 \cdot 10^{-3}$ and $1.48 \cdot 10^{-4}$, respectively, were found. Then, with the aid of these, the ionization constants of the bases investigated by us were calculated. Both methods gave practically identical results.

For acetone solutions in the majority of cases, neither the equilibrium constants of the indicators nor the ionization constants of the bases were known and we, therefore, employed only the above described method [6] for nonaqueous solutions. To determine the ionization constants, we employed the indicators bromophenol blue (maximal absorption of the basic form 5800 A), the transition constant of which was $K_i = 1.42 \cdot 10^{-5}$, and bromocresol purple (3800 A), the transition constant of which was $K_i = 2.86 \cdot 10^{-3}$. The maximum absorption in the alkine region and the transition constant of the indicator bromophenol blue were found in an acetone solution of c.p. potassium hydroxide and piperidine.

The same constants were found for the indicator bromocresol purple in connection with the base pachycarpine, isolated by us from pachycarpine sulfate and with a b.p. of 115° (3 mm) and a n_D^{20} 1.5310.

By conducting these measurements, we established that in acetone solutions, a regular change in ionization constants of the bases is observed with change in their concentration. Such a phenomenon was earlier noted by La Mer and Downes [7] and V. I. Dulova and N. V. Vostrilova [8, 9] during the determination of the ionization constants of acids using benzene and acetone as solvents. In the opinion of La-Mer and Downes, this phenomenon depended on the fact that association of the indicators and acids occurred in solvents with small dielectric constants. In carrying out the determinations in acetone solutions we employed the same method used in the work of V. I. Dulova and N. V. Vostrilova [8].

The measurements both in water and in acetone were conducted with the aid of an objective spectrophotometer [10].

In Table 1, the results of the measurements of the ionization constants of the organic bases investigated in water, using several indicators, are presented.

TABLE 1

Base	Indicator	Ionization constant of the base in water		pK_0
		according to the indicator	mean	
Lupinine	Tropeolin 000	$1.44 \cdot 10^{-4}$	$1.46 \cdot 10^{-4}$	3.84
	Thymol blue	$1.50 \cdot 10^{-4}$		
	Alizarin yellow	$1.43 \cdot 10^{-4}$		
Anabasine	Tropeolin 000	$1.27 \cdot 10^{-5}$	$1.54 \cdot 10^{-5}$	4.81
	Thymol blue	$1.68 \cdot 10^{-5}$		
	Alizarin red	$1.68 \cdot 10^{-5}$		
N-Methylanabasine	Tropeolin 000	$4.69 \cdot 10^{-6}$	$3.84 \cdot 10^{-6}$	5.42
	Thymol blue	$3.01 \cdot 10^{-6}$		
N-Nitrosoanabasine	Tropeolin 000	$2.27 \cdot 10^{-7}$	$2.46 \cdot 10^{-7}$	6.61
	Thymol blue	$2.66 \cdot 10^{-7}$		

As is evident from Table 1, lupinine is the strongest of the group of bases which we investigated. It can be classified as a base of medium strength as regards the magnitude of the ionization constant. From Table 1 it is also evident that the basicity of anabasine derivatives diminishes to a varying extent, depending on the nature of the substituent group.

The results of the determination of the ionization constants in acetone are presented in Table 2.

In Table 2, the values of pK_0 for aqueous solvents are presented for comparison; the corresponding values for nicotine, trimethylamine and piperidine were taken from the handbook tables [10]. The values

$$\Delta pK = pK_{0\,(\text{acetone})} - pK_{0\,(\text{water})}$$

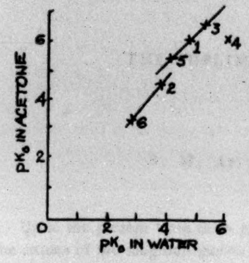
are plotted in the following graph.

TABLE 2

Base	K_0 (acetone)	pK_0 (acetone)	pK_0 (water)	$\Delta pK = pK_{\text{acetone}} - pK_{\text{water}}$
Lupinine	$3.06 \cdot 10^{-5}$	4.51	3.84	0.67
Anabasine	$9.06 \cdot 10^{-7}$	6.04	4.81	1.23
N-Methylanabasine	$2.28 \cdot 10^{-7}$	6.64	5.42	1.22
Nicotine	$7.10 \cdot 10^{-7}$	6.15	6.15	0.00
Trimethylamine	$4.30 \cdot 10^{-6}$	5.37	4.13	1.24
Piperidine	$5.15 \cdot 10^{-4}$	3.29	2.80	0.49

Comparison of the ionization constants of the bases in water and in acetone shows that acetone exerts a noticeable differentiating action on the bases.

In observing the differentiating action of acetone on acids, N. A. Izmailov and his co-workers in a series of works [11, 12] showed that the Brønsted theory was inadequate and did not in these circumstances explain the influence of acetone on acid strength. The differentiating action of acetone on acids was explained by N. A. Izmailov by the presence in the solutions of products of the reaction of the acids with the solvent. Using acetone as differentiating solvent, he succeeded in extending the titration limits of mixtures of acids, the strength of which in aqueous solutions [12] is close.



Dependence of the pK_0 of the bases in pure acetone on the pK_0 of these same bases in water. 1) Anabasine; 2) lupinine; 3) N-methylanabasine; 4) nicotine; 5) trimethylamine; 6) piperidine.

The figure plotted according to the data of Table 2 shows that in the case of acetone solutions of the bases investigated by us, deviations from the consequences of Brønsted's quantitative theory also occurred. The variations in the changes of strength of the bases in various solvents depending on the nature of the substance are evident from the graph following Table 2: ΔpK for anabasine and its derivatives is of the order of unity, for lupinine and piperidine is less than unity, and for nicotine the ionization constant is the same in water and acetone.

Comparison of the differentiating action of acetone on the strength of acids [9, 12, 13] and the bases investigated by us, permits the conclusion that the basicity is diminished much less than the strength of the majority of acids.

It is necessary to note that while a series of bases in acetone-water mixtures was studied by Pring [13], he did not note the differentiating action of acetone. Later N. A. Izmailov [12], reworking Pring's data, expressed the opinion that these data constitute evidence in favor of the differentiating action of acetone on bases. In this connection, our measurements, conducted on solutions of bases in pure acetone, are direct experimental confirmation of the differentiating action of acetone on bases.

The differentiating action of acetone on the bases studied was utilized for a separate conductometric titration in acetone solution of a mixture of anabasine and lupinine. Thus, mixtures of anabasine and nicotine could be separately titrated in acetone solution.

SUMMARY

1. The ionization constants of lupinine, anabasine, N-methylanabasine and N-nitrosoanabasine in water solution and of lupinine, anabasine, N-methylanabasine, nicotine, trimethylamine and piperidine in acetone solution were determined.

2. A differentiating action of pure acetone on the strength of the bases investigated was demonstrated.

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* See Consultants Bureau Translation, page 955.

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[illegible] the figure plotted [illegible] as a function of [illegible] Table shows that in the case of acetone solution of the [illegible] deviations from the conclusions of Izmailov's quantitative theory are observed. The variations in the strength of [illegible] of the bases in [illegible] depending on the nature of the solvent [illegible] from the graph following Table [illegible]. The bases [illegible] and piperidine [illegible] and [illegible] in [illegible] and acetone.

Comparison of the differentiating action of solvents on the strengths of [illegible] (Fig. [illegible]) and the [illegible] confirms the conclusion that the [illegible] than the strength of the majority of acids.

It is necessary to note that [illegible] bases in acetone-water mixtures was studied by [illegible] [15], he did not note the differentiating action of acetone [illegible] [16] [illegible] organic [illegible] that there [illegible] in favor of the differentiating action of [illegible] bases. In this connection, [illegible] experimental confirmation [illegible] differentiating action of acetone on bases.

Dependence of the pK_a of the bases in pure acetone on the pK_a of these same bases in water. 1) Aniline; 2) [illegible]; 3) N-methylaniline; 4) [illegible]; 5) [illegible]; 6) piperidine.

The differentiating action of acetone on the bases studied was utilized for a [illegible] tion in acetone solution of a mixture of aniline and [illegible]. The mixtures of aniline and [illegible] separately titrated in acetone solution.

SUMMARY

1. The ionization constants of [illegible] N-methylaniline and [illegible] in acetone solution [illegible] were determined.

2. A differentiating action of acetone on the strength of the bases investigated was demonstrated.

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THE SUBLIMATION ENTHALPY OF CHROMIC ANHYDRIDE AND OF MOLYBDIC ANHYDRIDE

S. M. Ariya, S. A. Shchukarev and V. B. Glushkova

Up to the present time there has been little in the way of data on the magnitude of the enthalpy of formation of the oxides of the subgroup metals in the gaseous state. At the same time these quantities,which in principle refer to simpler systems than the crystalline lattice,are of great interest as an aid to understanding the laws governing the magnitude of the heat of formation of binary compounds. The present work is devoted to the determination of the magnitudes of the sublimation enthalpies of molybdic and chromic anhydrides.

The sublimation enthalpy of MoO_3 was determined in 1941 by Kozo Uyeno [1]; he put forward the quantity $\Delta H_{928.1^\circ \text{ abs.}} = 63.7$ kcal/mole.

To determine the dependence of the vapor tension of $MoO_{3\,\text{cryst.}}$ on temperature we utilized the flow method. A narrow quartz tube filled with molybdic anhydride powder (purified by distillation in an oxygen stream) was placed in a ground joint in a wide quartz tube. The quartz tube was placed in a tubular furnace in such a fashion that the column of the preparation was in the constant temperature zone of the furnace. With the aid of a phototitration relay the temperature of the furnace was maintained constant to within ± 0.5°.

During the heating at the assigned temperature, dry air was drawn past the MoO_3 at a rate controlled with a rheometer. The quantity of air passing through the system was determined by the quantity of water which it displaced; the volume of water was measured with a measuring flask. The vaporized molybdic anhydride condensed in the cold part of the large quartz tube, where it was washed at the end of the experiment with a hot dilute solution of ammonia and subsequently was determined from the weight of MoO_3 formed.

Several experiments were performed at each temperature with varying rates of air flow. The rate of air passage, the further diminishing of which did not change the quantity of molybdic anhydride distilling (per liter of air), was made sufficiently rapid to satisfy the equation:

$$MoO_{\text{cryst.}} \rightleftharpoons MoO_{3\,\text{gas}}.$$

The data obtained are summarized in Table 1.

TABLE 1

Dependence of the Vapor Tension of MO_3 on Temperature

Temperature (°C)	Quantity of sublimate (in mg per liter of air)	P (in atmospheres)	log P
668	2.08	0.000324	$\bar{4}.51010$
668	2.19	0.000341	$\bar{4}.53248$
690.5	4.9	0.000763	$\bar{4}.88224$
690.5	4.4	0.000685	$\bar{4}.83549$
713.5	11.43	0.00178	$\bar{3}.25009$
713.5	11.78	0.00183	$\bar{3}.26319$

TABLE 2

Dependence of the Vapor Tension of CrO_3 on Temperature

Temperature (in °C)	Quantity of sublimate per liter of air (under unit conditions)
220	18.4
242	68.5
275	357.5

In Fig. 1, the logarithm of the equilibrium pressure (under unit conditions) is plotted as a function of the reciprocal value of the absolute temperature. It is evident from Fig. 1 that the values obtained fit well on a straight line.

If we put the values found by us in the generally known thermodynamic equation: $-RT \ln p = \Delta H - T\Delta S$, and assume that the magnitudes of the changes in enthalpy and entropy in the interval 668-714° C are constant, we find the following values for them:

$$\Delta H_{691°\,C} = 68.1 \pm 2.5 \text{ kcal/mole},$$

$$\Delta S_{691°\,C} = 56.9 \pm 2.6 \text{ kcal/mole}$$

Investigation of the vaporization process of chromic anhydride conducted in an apparatus similar to that described, showed that the vapor tension of chromic anhydride below its melting point is so low that it can not be measured. The data obtained for temperatures above the melting point are summarized in Table 2.

The sublimation enthalpy of chromic anhydride calculated from these data was equal to 28 kcal/mole (at 248° C). Since the precision of measurement was not high, this value had to be considered approximate.

The value obtained by us for the sublimation enthalpy of molybdic anhydride (68.1 kcal) exceeded by 4.4 kcal the value for the heat of vaporization of fused MoO_3 found by Kozo Uyeno (63.7 kcal). This value should have been greater than that found by the Japanese author by the value of the heat of fusion of molybdic anhydride, which Kelley [2] evaluated at 2.5 kcal. Thus, the discrepancy between the magnitudes found by us and by Kozo Yueno falls within the limits of experimental error. This provides a basis for accepting with confidence the value for the sublimation enthalpy of tungstic anhydride found by Kozo Yueno to be equal at $1368°_{abs.}$ to 112.6 kcal. There has been no publication concerning the value of the heat of sublimation of chromic anhydride prior to the present work; the value found by us, as has already been indicated above, is only approximate; however, in combination with the data for MoO_3 and WO_3, it gives a representation of the direction of the change in the values of the enthalpies of formation of the higher oxides of chromium and its analogs in the gaseous state.

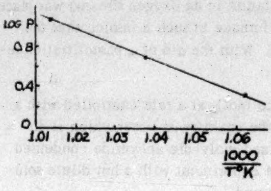

Fig. 1. Dependence of the logarithm of the vapor tension of $MoO_{3\,cryst}$ on the reciprocal of the values of the absolute temperature (under unit conditions).

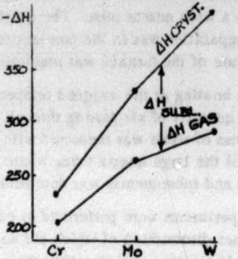

Fig. 2. Variation in the enthalpy of formation of crystalline and gaseous forms of the compounds MO_3 from the free atoms Cr, Mo, W and O_2.

TABLE 3*

Compound	$\Delta H_{form.}$ of the compounds MO_3 from the free metal atoms and O_2	
	in the gaseous state**	in the crystalline state
CrO_3	−204.3	−232.3
MoO_3	−263.4	−331.5
WO_3	−293.1	−405.7

In Table 3 are presented values for the enthalpies of formation of the gaseous and crystalline compounds of the type MO_3 from the free atoms of the corresponding elements and molecular oxygen.

The data presented in Table 3 and Fig. 2 show that during the transition from chromium to tungsten, the value for the enthalpy of formation increases both for the gaseous and for the crystalline forms; the latter increases considerably faster, however.

S. A. Shchukarev [3] recently indicated that the direction of change of the enthalpy of formation of binary compounds is frequently opposite to the direction of change of the sum of a number of ionization potentials which is equal to the valency of the homologous elements.

Fig. 2 illustrates the working of this rule in the case of the materials considered by us (the sum of the 6 ionization potentials falls from Cr to W). It seems to be natural that the rate of increase of the enthalpy of formation of the crystalline forms (in comparison with the enthalpy of formation of the gaseous forms) should become more rapid as the sum of the homologous ionization potentials diminishes.

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* We did not convert the data on the sublimation heat of MO_3 to one common temperature on account of the absence of data on the heat capacities. This can not distort the direction of the change in ΔH during the transition from Cr to W. For similar reasons, we did not make a correction for the heat of fusion of CrO_3.

** The values for the sublimation enthalpies of Cr, Mo and W and the enthalpies of formation of their higher oxides in the crystalline state are taken from a compilation of thermal constants [2].

The bond in the oxygen compounds should assume an ionic character as a consequence of the diminishing of the values of the ionization energy of the atoms; this in turn leads to strengthening of the metal-oxygen bond, both in the gaseous molecules and in the crystalline lattice. It must, naturally, be more significant in the latter case, since particles not in direct contact with each other can react in the crystalline lattice. The observed increase in the values of the sublimation enthalpies of the higher oxides as one moves down subgroup VI is a necessary consequence of this.

In other words, it can be concluded that the magnitudes of the sublimation enthalpies of the higher oxides of the elements of the subgroups should vary reciprocally with the energy of formation of the ions of homologous charge (equal valence).

The data on the values of the sublimation enthalpies of the higher oxides of the elements of the subgroup are still very meager, but it is known qualitatively that during progress downward in subgroups V and VII of the periodic system, the oxides are less volatile. The total ionization work also diminishes as one progresses down in the subgroup.

SUMMARY

1. The sublimation enthalpy of molybdic anhydride was found equal (at 691° C) to 68.1 ± 2.5 kcal/mole.

2. The sublimation enthalpy of chromic anhydride was found to be approximately equal to 28 kcal/mole.

3. The sublimation enthalpy of the higher oxides of the elements of subgroup VI of the periodic table changes reciprocally with the total of the six ionization potentials of these elements.

It can be assumed that this rule is of a general character.

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INVESTIGATION OF THE REACTION OF COMPLEX FORMATION BY THE CUPRIC ION WITH THE IONS OF CITRIC ACID

O. D. Talalaeva and A. S. Tikhonov

The ions of citric acid can form complex compounds with many metallic ions that are readily soluble in water over a broad pH range. This property of citric acid complexes is widely utilized in chemical analysis, and in the isolation of the rare earths and the transuranium elements [1-2].

In view of the fact that at the present time no attention has been paid to the process of complex formation between citric acid and metallic ions [3, 4, 5, 11], we investigated these complex formation reactions and took account of the pH of the medium and the acid-base functional groups of cupric hydroxide and citric acid.

Cupric hydroxide forms at a pH of 5.3-6.9; it is distinctly amphoteric, giving rise to cuprites in alkaline medium. There are contradictory notices in the literature concerning the solubility of $Cu(OH)_2$; this is explained by the small extent to which it has been studied.

The most reliable data on the solubility product of copper hydroxide is the value $K_s = 5.6 \cdot 10^{-20}$ [5].

Citric acid, as a tribasic acid, has accordingly three ionization constants:

$$K_1 = 8.4 \cdot 10^{-4},\ K_2 = 1.8 \cdot 10^{-5} \text{ and } K_3 = 4.0 \cdot 10^{-6} \text{ [6].}$$

Inasmuch as all three ionization constants of citric acid have close numerical values, within the limits pH 1-8 in an aqueous solution equilibrium of the four following forms will occur:

$$H_3C_6H_5O_7 \rightleftharpoons H_2C_6H_5O_7^{-1} \rightleftharpoons HC_6H_5O_7^{-2} \rightleftharpoons C_6H_5O_7^{-3}.$$

In the presence of a total concentration of citric acid in a solution of S moles/liter, the concentration of each of its forms can be calculated according to the following equations:

$$[H_3C_6H_5O_7] = \frac{S}{1 + \frac{K_1}{[H^{\cdot}]} + \frac{K_1K_2}{[H^{\cdot}]^2} + \frac{K_1K_2K_3}{[H^{\cdot}]^3}}, \qquad (1)$$

$$[H_2C_6H_5O_7^{-1}] = \frac{S}{1 + \frac{[H]}{K_1} + \frac{K_2}{[H^{\cdot}]} + \frac{K_2K_3}{[H^{\cdot}]^2}}, \qquad (2)$$

$$[HC_6H_5O_7^{-2}] = \frac{S}{1 + \frac{[H^{\cdot}]}{K_2} + \frac{K_3}{[H^{\cdot}]} + \frac{[H^{\cdot}]^2}{K_1K_2}}, \qquad (3)$$

$$[C_6H_5O_7^{-3}] = \frac{S}{1 + \frac{[H^{\cdot}]}{K_3} + \frac{[H^{\cdot}]^2}{K_2K_3} + \frac{[H^{\cdot}]^3}{K_1K_2K_3}}. \qquad (4)$$

The amount of each form of the citric acid anion depending on the pH of the medium is portrayed graphically in Fig. 1.

All three citric acid anions can form complex ions with the cupric ion [11], but the anion $C_6H_5O_3^{-3}$, as the ion of the weakest acid and the greatest charge, will be able to yield the strongest bond. This principle is in excellent agreement with the results of our investigations.

These investigations were conducted by the methods of photometry, solubility and the visual-volumetric method in the pH interval 1-14. Determination of the pH was made with a glass electrode and an LP-5 potentiometer.

The photometric investigations were conducted on a Pulfrich photometer with the characteristic light filters:

No. of light filter	I	II	III	IV	V	VI	VII	VIII	IX
Wave length λ (in A)	7500	7260	6650	6190	5740	5330	4960	4650	4280

The absorption curves obtained for a solution of pure copper sulfate and for a solution of copper sulfate in the presence of sodium citrate at various pH values, showed that the optical density and character of the absorption markedly changed with changes of the pH of the medium.

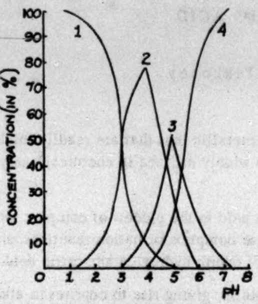

Fig. 1. Comparative content of the various citric acid ions in relation to the pH of the medium. 1) $H_3C_6H_5O_7$; 2) $H_2C_6H_5O_7^{-1}$; 3) $HC_6H_5O_7^{-2}$; 4) $C_6H_5O_7^{-3}$.

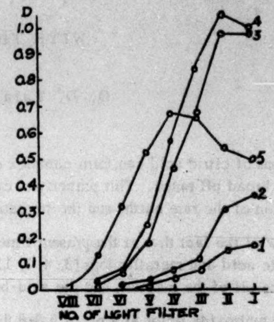

Fig. 2. Absorption curves of a solution of $CuSO_4$ in the presence and in the absence of citric acid, in relation to the pH of the medium. 1) 0.02 mole/liter of $CuSO_4$; 2) 0.02 mole/liter of $CuSO_4$ + 0.1 mole/liter of $H_3C_6H_5O_7$, pH 2.3; 3) 0.02 mole/liter of $CuSO_4$ + 0.1 mole/liter of $H_3C_6H_5O_7$, pH 4.4; 4) 0.02 mole/liter of $CuSO_4$ + 0.1 mole/liter of $H_3C_6H_5O_7$, pH 12.2; 5) $CuSO_4$ in 3 mole/liter of KOH.

Introduction of citric acid ions into $CuSO_4$ solution markedly increases the optical density of the solution (Fig. 2), which indicates complex formation between the copper ion and the citric acid ions. Change in the pH of the solution changes the character of the absorption. At pH 4-12 the maximum absorption is found in the long wave portion of the spectrum −light filters I and II (Curves 1, 2, and 3, Fig. 2). At pH approximately equal to 12 the absorption maximum is displaced toward the short wave portion of the spectrum −light filters II and IV (Curves 4 and 5, Fig. 2).

On the basis of the experimental data (Fig. 2) it can be concluded that the most sensitive light filters for the study of the citric acid complexes of copper will be: I (7500 A), II (7260 A) and, in part, III (6650 A).

Photometric investigations of solutions containing $CuSO_4$ = 0.02 mole/liter and $H_3C_6H_5O_7$ = 0.10 mole/liter at varying values of the pH of the medium show that, beginning with pH 2 and greater, the optical density is markedly increased, reaching a maximum value at pH approximately equal to 5-6 and then remaining constant up to pH ≈ 12. At pH > 12, the optical density is markedly lowered and in solutions at small $C_6H_5O_7^{-3}$ content, the formation of a CuO precipitate is sometimes observed.

The increased optical density of solutions at pH 2 and higher is doubtless associated with the conversion of citric acid into the anions $H_2C_6H_5O_7^{-1}$, $HC_6H_5O_7^{-2}$ and $C_6H_5O_7^{-3}$ (Fig. 1), which enter into reaction with the copper ion and form complexes. If the fact that the conversion of citric acid into the corresponding anions proceeds in the pH interval 2-7 and coincides with the pH of formation of cupric hydroxide is taken into account, one will expect to find a multicomponent system in the solution, the equilibrium state of which is determined by the pH value in each separate instance.

If we compare Figs. 1 and 3, we see that the increase in optical density of the solutions of copper in the presence of citric acid observed at pH 2-3 is associated with reciprocal reaction of the cupric ion with the $H_2C_6H_5O_7^{-1}$ ion, with the formation of a complex ion of the possible composition

$$Cu(H_2C_6H_5O_7)^{+1}.$$

The sharp increase in the optical density at pH ≈ 3-5 is associated with the formation of $H_2C_6H_5O_7^{-1}$ in solution in addition to the $HC_6H_5O_7^{-2}$ ions, the latter, entering into reaction with the $Cu(H_2C_6H_5O_7)^{+1}$ ion give a stronger compound.

To resolve the problem of how the copper ion reacts with the $H_2C_6H_5O_7^{-1}$ and $HC_6H_5O_7^{-2}$ ions and how the complex is formed, photometric profiles at pH 4.5 for a solution with a $CuSO_4$ concentration of 0.02 mole/liter and varying quantities of $Na_3C_6H_5O_7$ were made. The value of pH 4.5 was selected because, in the first place, at this pH value, a sharp increase in the optical density is observed (Fig. 3), and, in the second place, all four forms of the citric acid anions are present in solution. In establishing the dependence of the optical density on the content of any of the citric acid ions by way of the changes of the general quantity of $Na_3C_6H_5O_7$, we have solved the problem of the composition of the complex at this pH value of the medium.

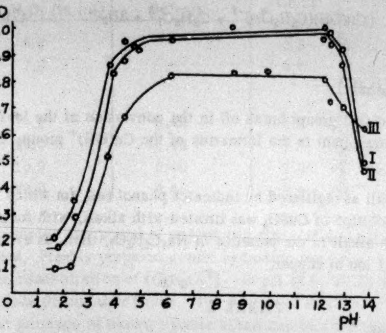

Fig. 3. Dependence of the optical density (D) of a solution of 0.02 mole/liter of $CuSO_4$ and 0.1 mole/liter of citric acid on the pH of the medium. I, II, III = number of light filter used.

In Fig. 4 the dependence of the optical density of the copper solution on the content of the ions $H_2C_6H_5O_7^{-1}$ and $HC_6H_5O_7^{-2}$ is presented. It can be concluded from the data of Fig. 4 that the maximum optical density at pH 4.5 is reached when there is 1 ion of $H_2C_6H_5O_7^{-1}$ and 1 ion of $HC_6H_5O_7^{-2}$ for 1 ion of copper. Starting from the indicated correlation, one can write down the following composition for the citric acid complex of copper existing in the pH range ≈ 3-5:

$$[Cu(H_2C_6H_5O_7)(HC_6H_5O_7)]^{-1}.$$

The formation of this complex ion can be compared with the process of the conversion of citric acid into the corresponding anions during the increase of the pH of the medium: $Cu^{+2} + H_2C_6H_5O_7^{-1} \rightleftharpoons Cu(H_2C_6H_5O_7)^{+1}$ at pH ≈ 2-3 and at pH ≈ 3-5:

$$(CuH_2C_6H_5O_7)^{+1} + HC_6H_5O_7^{-2} \rightleftharpoons [Cu(H_2C_6H_5O_7)(HC_6H_5O_7)]^{-1}.$$

In addition to our investigations, there are indications in the literature regarding the existence of the specified complex ion [3].

We attempted to calculate the instability constant of this complex ion from the photometric measurements by means of equation (5)

$$K_{\text{inst.}} = \frac{[Cu^{+2}][H_2C_6H_5O_7^{-1}][HC_6H_5O_7^{-2}]}{[\text{complex}]}. \qquad (5)$$

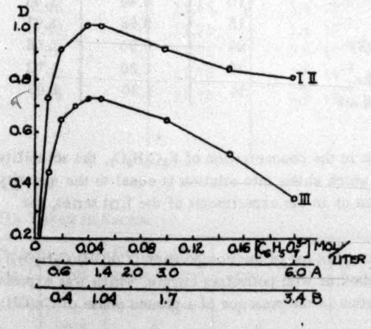

Fig. 4. Dependence of the optical density (D) of an 0.02 mole/liter solution of $CuSO_4$ on the ratios of the anions $A = \frac{[H_2C_6H_5O_7^{-1}]}{[Cu^{+2}]}$, $B = \frac{[HC_6H_5O_7^{-2}]}{[Cu^{+2}]}$ at pH 4.5. I, II, III = number of light filter.

In this equation the concentrations of $[H_2C_6H_5O_7^{-1}]$ and $[HC_6H_5O_7^{-2}]$ in equilibrium with the complex are determined by the total concentration of the salt $Na_3C_6H_5O_7$ and the pH of the medium; the concentration of the complex* is calculated according to the equation (6), well-known in the literature [7-10]

$$[\text{complex}] = \frac{D - E_1[Cu^{+2}]_{\text{total}}}{E_2 - E_1} \qquad (6)$$

The equilibrium concentration of the copper ion $[Cu^{+2}]$ is determined as the difference $[Cu^{+2}]_{\text{total}} - [\text{complex}] = [Cu^{+2}]$. The value of the molecular extinction coefficient for $CuSO_4 - E_1 = 8.5$ (determined with light filter II) and the value for the molecular extinction coefficient for the complex ion $[Cu(H_2C_6H_5O_7)(HC_6H_5O_7)]^{-1} - E_2 = 52.5$.

The mean value of the instability constant of this complex ion was of the order of magnitude of 10^{-4}.

Inasmuch as the stability of the complex ion $[Cu(H_2C_6H_5O_7)(HC_6H_5C_7]^{-1}$ is not great and, according to the numerical value of $K_{\text{inst.}}$ is close to the 1st and 2nd ionization constants of citric acid, during the increase of the pH of the medium the ions $H_2C_6H_5O_7^{-1}$ and $HC_6H_5O_7^{-2}$ entering into the complex will consequently be converted into $C_6H_5O_7^{-3}$ and the complex ion $[CuH_2C_6H_5O_7)(HC_6H_5O_7)]^{-1}$ must be converted into a new compound. The conversion of $H_2C_6H_5O_7^{-1}$ and $HC_6H_5O_7^{-2}$ into $C_6H_5O_7^{-3}$ is practically complete at pH 7. At pH 5.3, however, the copper ion begins to react with the OH' ion, forming a difficultly soluble hydroxide. In the presence of these citric acid ions, cupric hydroxide is not formed, but the optical density of the solution is increased; consequently, the complex ion $[Cu(H_2C_6H_5O_7)(HC_6H_5O_7)]^{-1}$ is converted into a new compound, which has a stability equal to or greater than the stability of cupric hydroxide.

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* Designated as [complex].

By the visual titration method and the solubility method it was established that at pH 5.3-7 a complex ion of the composition $[Cu(OH)(C_6H_5O_7)]^{-3}$ is formed. The chemistry of the conversion of the ion $[Cu(H_2C_6H_5O_7)(HC_6H_5O_7)]^{-1}$ into the complex ion $[Cu(OH)(C_6H_5O_7)]^{-2}$ can be represented by Equation (7).

$$[Cu(H_2C_6H_5O_7)(HC_6H_5O_7)]^{-1} + 4OH' \rightleftharpoons [Cu(OH)(C_6H_5O_7)]^{-2} + C_6H_5O_7^{-3} + 3H_2O. \tag{7}$$

It is evident from this equation that the complex ion

$$[Cu(H_2C_6H_5O_7)(HC_6H_5O_7)]^{-1}$$

can be considered as a tetrabasic acid in which 3 equivalent OH' groups break off in the conversion of the ions $H_2C_6H_5O_7^{-1}$ and $CH_6H_5O_7^{-2}$ into the ion $C_6H_5O_7^{-3}$ and 1 equivalent in the formation of the $Cu(OH)^+$ group; this is confirmed by the experimental data.

1. A pure solution of $Na_3C_6H_5O_7$ does not consume alkali as registered by indicator phenol red, for which the interval of color transformation lies at pH 6.8-8.0. A solution of $CuSO_4$ was titrated with alkali, with formation of $Cu(OH)_2$. If the same $CuSO_4$ solution is titrated with alkali in the presence of $Na_3C_6H_5O_7$, then, as evidenced by phenol red, only 1 equivalent of alkali is consumed for 1 ion of copper.

The results of the titrations are presented in Table 1.

TABLE 1

Titration of a Solution of $Na_3C_6H_5O_7$ with 0.1 M solution of NaOH. In each test, 10 ml of $Na_3C_6H_5O_7$ was used.

Amount of 0.02 M $CuSO_4$ (ml)	Consumed 0.474 N NaOH (ml)	$\frac{[OH^-]}{[Cu^{+2}]}$
10	0.45	1.05
10	0.45	1.05
15	0.68	1.07
20	0.90	1.06
30	1.30	1.02
30	1.30	1.02

By precisely the same titration with the indicator phenol red, the quantity of $C_6H_5O_7^{-3}$ ions entering into the copper complex was established (Table 2)

The data of Tables 1 and 2 serve to support the conclusion that in the complex ion $[Cu(OH)(C_6H_5O_7)]^{-2}$ for 1 ion of Cu^{+2}, 1 OH' ion and 1 ion of $C_6H_5O_7^{-3}$ are actually matched.

2. A solution of 0.1 mole/liter of $K_3C_6H_5O_7$ has a pH of 7.4; the solution over a precipitate of $Cu(OH)_2$ has a pH of 6.49. If the same $Cu(OH)_2$ precipitate is dissolved in $K_3C_6H_5O_7$, then a solution with a pH of 11.7 is obtained. This points to the following chemistry for the reaction:

$$Cu(OH)_2 + C_6H_5O_7^{-3} \rightleftharpoons [Cu(OH)\cdot(C_6H_5O_7)]^{-2} + OH' \tag{8}$$

Quantitative investigations in the study of the chemistry of the reactions of $Cu(OH)_2$ with $K_3C_6H_5O_7$ by the solubility method are presented in Table 3.

It follows from the data of Table 3 that with the increase in the concentration of $K_3C_6H_5O_7$, the solubility of the cupric hydroxide is increased and the quantity of copper which enters into solution is equal to the quantity of alkali formed in the solution. In all these experiments, just as in the experiments of the first series, the ratio $[OH^-]/[Cu^{+2}]$ was close to unity.

Thus, in the pH interval of approximately 7.0-11.0, a complex ion of the composition $[Cu(OH)(C_6H_5O_7)]^{-2}$ exists. Proceeding from the reciprocal reaction of cupric hydroxide with potassium citrate, which was expressed by Equation (8), we find the equilibrium constant of this reaction in the presence of a ground phase of $Cu(OH)_2$ to be equal to

$$K_{eq_1} = \frac{[Cu(OH)(C_6H_5O_7)^{-2}][OH']}{[C_6H_5O_7^{-3}]} \tag{9}$$

For the complex ion $[Cu(OH)(C_6H_5O_7)]^{-2}$, existing at pH approximately 7-11, the ionization constant is expressed by Equation (10)

$$K_i = \frac{[Cu^{+2}][OH'][C_6H_5O_7)^{-3}]}{[Cu(OH)(C_6H_5O_7)^{-2}} \tag{10}$$

By combining Equations (10) and (9) we can readily show that

$$K_{inst.} = \frac{K_{SCu(OH)_2}}{K_{eq_1}}.$$

TABLE 2

Titration of a Solution of $Na_3C_6H_5O_7$ with NaOH Solution. In each case 10 ml of 0.02 mole/liter $CuSO_4$ solution was introduced.

Amount taken of 0.02 mole/liter $Na_3C_6H_5O_7$ (in ml)	Amount of 0.474 NaOH consumed (in ml)	$\frac{[C_6H_5O_7^{-3}]}{[Cu^{+2}]}$	Comment
5.0	–	0.5	The solution became turbid from $Cu(OH)_2$ formation
7.0	–	0.7	
10.0	0.42	1.0	The solution remained transparent
10.0	0.45	1.0	
10.0	0.45	1.0	
20.0	0.45	2.0	

At a numerical value of $K_{sCu(OH)_2} = 5.6 \cdot 10^{-20}$ and a mean value of $K_{eq_1} = 1.24 \cdot 10^{-3}$, the value of $K_{inst} = 4.5 \cdot 10^{-17}$.

If 2 equivalents of alkali for one of copper are introduced into a solution containing hydrated cupric ions, then for each mole of copper contained in the solution 2 moles of sodium or potassium citrate are required, that is, the following ratio must be observed

$$\frac{[OH']}{[Cu^{+2}]} = \frac{[C_6H_5O_7^{-3}]}{[Cu^{+2}]} = 2.$$

Such a solution has a pH of 12.5.

To determine the composition of the complex compound of copper and citric acid at pH = 12.5, investigations were conducted by the solubility method. Freshly prepared cupric hydroxide was taken as ground phase and its solubility was determined in relation to the concentration of $(C_6H_5O_7^{-3}]$ at pH 12.5, which was established by the addition of KOH regulated by glass electrode pH measurements. The process of solution of cupric hydroxide in the presence of potassium citrate and in the presence of excess caustic alkali can be expressed by the equation (11)

$$Cu(OH)_2 + yC_6H_5O_7^{-3} \rightleftharpoons [Cu(OH)_2(C_6H_5O_7)_y]^{-3y}. \tag{11}$$

TABLE 3

Reaction of $Cu(OH)_2$ with $K_3C_6H_5O_7$. $Cu(OH)_2$ taken in excess

Amount of $K_3C_6H_5O_7$ introduced (in mole / liter)	pH	Amount of back-titrated alkali according to phenol red (in mole /liter)	Copper found in solution (in mole /liter)	$\frac{[Cu^{+2}]}{[OH']}$	K_{eq_1}
0.05	11.65	$1.4 \cdot 10^{-2}$	$1.69 \cdot 10^{-2}$	1.2	$2.2 \cdot 10^{-3}$
0.10	11.75	$1.8 \cdot 10^{-2}$	$1.99 \cdot 10^{-2}$	1.1	$1.4 \cdot 10^{-3}$
0.15	11.75	$2.0 \cdot 10^{-2}$	$2.12 \cdot 10^{-2}$	1.01	$0.92 \cdot 10^{-3}$
0.20	11.75	$1.8 \cdot 10^{-2}$	$2.06 \cdot 10^{-2}$	1.1	$0.64 \cdot 10^{-3}$
0.25	11.75	$3.9 \cdot 10^{-2}$	$4.01 \cdot 10^{-2}$	1.0	$1.07 \cdot 10^{-3}$
			Average	1.0	$1.24 \cdot 10^{-3}$

TABLE 4

$Cu(OH)_2$ Taken in Excess

$K_3C_6H_5O_7$ in mole / liter	pH	Cu (in g/25 mole /liter)	$[Cu^{+2}]$ mole /liter	$K_{eq_2} = \frac{\text{Conc. of the complex}}{[C_6H_5O_7^{-3}]^2}$
0.01	12.5	0	0	–
0.03	12.6	0.0005	0.00031	$3.6 \cdot 10^{-1}$
0.05	12.6	0.001	0.00062	$2.48 \cdot 10^{-1}$
0.07	12.3	0.0026	0.00163	$3.30 \cdot 10^{-1}$
0.10	12.1	0.0032	0.002	$2.00 \cdot 10^{-1}$
0.12	12.5	0.0071	0.0045	$3.12 \cdot 10^{-1}$
0.14	12.5	0.0097	0.0061	$3.10 \cdot 10^{-1}$
0.15	12.7	0.0144	0.009	$4.00 \cdot 10^{-1}$
0.17	12.5	0.0154	0.0098	$3.40 \cdot 10^{-1}$
0.20	12.3	0.0208	0.013	$3.25 \cdot 10^{-1}$
0.22	12.5	0.0204	0.0128	$2.60 \cdot 10^{-1}$
0.25	12.5	0.0264	0.0165	$2.60 \cdot 10^{-1}$
		Mean value		$3.30 \cdot 10^{-1}$

At a constant alkalinity of the medium the equilibrium constant of reaction (11) will be expressed by equation (12)

$$K_{eq_2} = \frac{[Cu(OH)_2(C_6H_5O_7)_y]^{-3y}}{[C_6H_5O_7^{-3}]^y} \tag{12}$$

Given a series of analogous measurements of the solubility of $Cu(OH)_2$ (Table 4) as a function of the concentration of $[C_6H_5O_7^{-3}]$, we can take any two of them to find a value y which will be determined by the equation (13)

$$y = \frac{\Delta \log[\text{complex}]}{\Delta \log[C_6H_5O_7^{-3}]}. \tag{13}$$

The quantity of copper entering into solution is adopted as the concentration of the [complex] on the assumption that the solubility of the copper hydroxide depends only on complex formation according to equation (11).

$\underline{y}$ is enumerated according to equation (13) from the data of Table 4, the mean value of which is equal to 2. This implies that at a pH ≤ 12.5 the complex ion has the composition: $[Cu(OH)_2(C_6H_5O_7)_2]^{-6}$. The instability constant of this complex ion can be calculated according to equation (14)

$$K_{inst._2} = \frac{K_S Cu(OH)_2}{K_{eq_2}} \quad (14)$$

Equation (14) is obtained by simple transformation of equation (12) and the equation of the ionization constant of the complex ion $[Cu(OH)_2(C_6H_5O_7)_2]^{-6}$. The mean value of this instability constant at $K_{S Cu(OH)_2} = 5.6 \cdot 10^{-20}$ and at $K_{eq_2} = 3.30 \cdot 10^{-1}$ will be equal to $1.7 \cdot 10^{-19}$.

SUMMARY

1. The formation of a complex between the cupric ion and the ions of citric acid in the pH interval 1-14 was studied by the methods of photometry, solubility and visual titration.

2. It was established that in aqueous medium the composition of the complex compound of the cupric ion with the ions of citric acid changes, depending on the pH of the medium.

3. In acidic medium at pH ≈ 2-5, there exists a complex ion of composition $[Cu(H_2C_6H_5O_7)(HC_6H_5O_7)]^{-1}$ with an instability constant equal to 10^{-4}.

4. At pH ≈ 7.0-11.5 there exists a complex ion of the composition $[Cu(OH)(C_6H_5O_7)]^{-2}$ with $K_{inst.} = 10^{-17}$.

5. At pH ≤ 12.0 there exists a complex ion of the composition $[Cu(OH)_2(C_6H_5O_7)_2]^{-6}$ with a $K_{inst.} = 10^{-19}$.

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CONCERNING CERTAIN QUESTIONS OF RUSSIAN NOMENCLATURE IN SILICO-ORGANIC CHEMISTRY

A DISCUSSION

M. G. Voronkov

In the present note we wish to dwell on certain unsettled questions concerning Russian terminology in the chemistry of silico-organic* compounds. First of all, it should be indicated that the very term "silico-organic" (silico-organic compounds, silico-organic chemistry and so forth) is used ambiguously in the Russian literature. Many Russian chemists (N. A. Menshutkin [1], A. N. Nesmeyanov [2], B. N. Dolgov [3, 4], M. G. Voronkov [4, 5] and others) confine themselves to the version of this term indicated above. At the same time, a number of Soviet silico-organic chemists (K. A. Andrianov, A. V. Topchiev, A. Ya. Yakubovich and others) use the term "silici-organic" in their works. Certain authors (A. P. Kreshkov) use either version of this term.

The need for a uniform Russian chemical terminology excludes so ambiguous a way of writing a single term. It is not difficult to demonstrate that the first of the methods set forth for transcribing the term "silico-organic" is uniquely correct. In the first place, for a whole century, all silicon derivatives have been denoted in Russian chemical terminology by the prefix "silico-" (and not by the prefix "silici"). In the Russian literature one meets only with the uniformly transcribed forms of such silicon derivatives as silico-earths, silico-polymers, silico-hydrocarbons, silico-rubbers, silico-hydrofluoric acid, silico-ethyl ether, silico-chloroform, silico-hydride** etc., etc.. Moreover, the very term "silico-organic" (silico-organic compounds) appeared as such in the Russian literature in 1884 (N. A. Menshutkin [1]). This term was employed in an unchanged form in all Russian works and not until 1937-1939 in articles by G. V. Medoks [7] and K. A. Andrianov [8] did there appear another, discrepant transcription of this term, a transcription the use of which has regrettably become rather wide spread.

In the second place, the historically laid down and established transcription of the term "silico-organic" appears to be uniquely correct from a grammatical point of view. As is well-known, in the formation of complex words from their roots, they are united by the connecting vowels o and e. We say "elemento-organic", "metallo-organic" compounds, but not "elementorganic", "metallorganic". The existence in the Russian chemical terminology of the terms "magnesiorganic", "lithiorganic" and so forth (which are always alluded to on behalf of the application of the term "silici-organic"), is explained only by their unpronounceableness and dissonance in comparison with the other, grammatically more correct, method of transcription.

All the above indicates that the term "silico-organic" is uniquely correct and that other transcriptions of it should no longer appear in our literature.

We further consider that the use of the un-Russian prefix "siliko" to denote derivatives of silicon, which regretably still has a place in the works of certain authors (A. D. Petrov, A. I. Brodsky and others), is inadmissable. The mellifluous Russian prefix "kremne", profoundly rooted in our terminology, exists for this purpose. We remind the reader that D. I. Mendeleev [6, 9] always employed the Russian —"kremne" in place of the German prefix "siliko". Therefore, not "siliko-chloroform", "siliko-halogens" and so forth, but "kremne-chloroform", "kremne halogens" should be written.

Also completely inadmissible in our literature is the German word "silitsy" still employed in place of the Russian word "kremny". Consequently, the term "ferro-kremny" should be employed in place of the often used term "ferrosilitsy".***

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* The Russian word for silicon is kremny. The following equivalents have been used to render the terms employed in the ensuing discussion: "kremne-" =silico-; "kremni" = silici-; "siliko-" = siliko. The Russian prefixes have been transliterated in the discussions of euphony and pronounceableness.

** The last three terms were introduced into Russian terminology by D. I. Mendeleev [6].

*** The prefix "ferro" is often employed in Russian chemical and metallurgical terminology, and it is inappropriate to have to utter such an unpronounceable term as "zhelezokremny".

At the same time, to change such terms as "silitsides" or silikates" appears irrational to us.

The irregular foreign term "silicone" to denote silico-organic polymers has fortunately not taken root in the Russian literature.* However, in rare cases one encounters its use, which is unconditionally inadmissable. The term employed in the USSR, "polysiloxanic polymers" appears to be the most correct, inasmuch as it actually reflects the structure of these polymers. It is also necessary to recognize the very successful Russian terms "kremne-polymers" and "kremne-rubbers".

In recent years, the terms " silicon tetrachloride", "silicon tetrafluoride" and so forth, have taken root in the Russian literature. The use of such long designations appears hardly advisable. Such forms as "monochloride", "dichloride", or such a thing as "polychlorides of silicon" and so forth, certainly do not exist. Therefore, we consider the use of the shorter and more easily pronounceable terms: "silicon chloride", "silicon fluoride", "silicon bromide" and so forth, to be necessary, as did D. I. Mendeleev [6, 9], A. M. Butlerov [10] and N. A. Menshutkin [1]. We also consider it necessary to change such strange, incorrect and prolix names as "the ethyl ester of orthosilicic acid" etc. into shorter and mellifluous terms such as "silico-ethyl ether", etc., introduced into our terminology by D. I. Mendeleev [6].

Inasmuch as the chemistry of silico-organic compounds has become an independent division of chemical science in recent years, it is time to denote it in the Russian literature by the term "silico-organic" chemistry. This term was employed for the first time by us in 1952 [5] and subsequently won recognition (A. N. Nesmeyanov [2]).

In our opinion, it would have been reasonable to distinguish the terms "silico-organic compounds" and "organic compounds of silicon" as referring to two different concepts. By "silico-organic compounds" one ought to understand all compounds of silicon, except the silicates (and a majority of the silicides) [4, 5], just as the term organic compounds indicates all carbon compounds except the carbonates (and a majority of the carbides). Thus, such inorganic compounds of silicon as $SiCl_4$, $HSiCl_3$, Si_2H_6, $FSiH_3$, $(H_3Si)_2O$, $N(SiH_3)_2$ etc., not even to mention such compounds as $Si(OCH_3)_4$, $(C_4H_9S)_3SiNH_2$, etc., **should be included among the "silico-organic compounds". At the same time, only the compounds of silicon which contain organic radicals and perhaps also (this does not, in our opinion, appear necessary) compounds which contain even one Si–C bond should be included among the "organic compounds of silicon".

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* As early as the last century [3, 6] the term "silicone" denoted one of the products of the action of HCl on calcium silicide in our literature.

** Here our point of view coincides with that of A. D. Petrov [11].

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